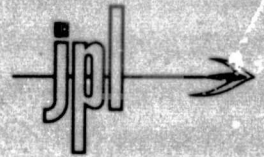


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The Boeing Company  
Report D180-19046-2



**THE CADMIUM ELECTRODE  
REVIEW OF THE STATUS OF RESEARCH**

September 1976

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## PREFACE

In JPL's effort to improve the life of the sealed nickel-cadmium battery, it was surmized that one of the primary life-limiting factors of the system was due to the degradation of the cadmium electrode. Therefore, as a follow-on to the Battery Literature Search, the Boeing Company was assigned the task of reviewing and summarizing the findings of research work on cadmium electrodes. No attempt was made to critically evaluate the referenced articles, since this report was initially intended for internal use. Other people, however, have expressed a desire to obtain a copy; therefore, the report was published for distribution to the public.

The report was not edited by JPL, and its content is not necessarily endorsed by the Jet Propulsion Laboratory, California Institute of Technology or the National Aeronautics and Space Administration.

R. S. Bogner  
JPL Project Manager

## **ACKNOWLEDGEMENT**

**A. Uchiyama and S. Bogner were technical monitors for the Jet Propulsion Laboratory on this contract. The contribution of many technical discussions is gratefully acknowledged.**



## ABSTRACT

This report is a condensation of recent research characterizing the negative cadmium electrode used in a nickel-cadmium battery cell. It is intended to provide a worker in the field a summary of important information about the cadmium electrode with citations to references where more detailed information is available. In collecting research information, emphasis has been placed on data pertinent to aerospace applications. An evaluation of some of the published results of cadmium electrode research is included.

# THE CADMIUM ELECTRODE

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## 1.0 INTRODUCTION AND SUMMARY

This document summarizes the results of recent research characterizing the negative cadmium electrode in a nickel-cadmium battery cell. The intent is to provide the worker in the field a summary of important information in all pertinent aspects of the cadmium electrode, with citations to references from which he can obtain all available detailed information. This document does not contain application information except where it is useful to understanding of electrode behavior or to illustrate the effects of selected design variables.

An attempt has been made in the text to evaluate some of the published results of cadmium-electrode research. For example, consider passivation, an important phenomenon, affecting the capacity of nickel-cadmium cells. Researchers disagree on the mechanism for passivation, hence a valid explanation will require additional work with more sophisticated techniques and equipment. On the other hand, there are areas where evaluation of the published data is clearly beyond the scope of this document. One such area is manufacturing methods where there are involved sophisticated processes incorporating much proprietary data and undocumented experience.

No attempt has been made to provide a critique of today's cadmium electrode technology or to identify the most worthwhile research projects. However, where conflicting information was found in the literature, or where important gaps in technology were apparent, then this has been pointed out in the final section on conclusions.

In this document the terms "anodization" and "oxidation" are used synonymously to describe phenomena occurring during discharging of the cadmium electrode. Often different authors use different words for the same phenomenon--we have tried to relate such words wherever possible. Detailed abstracts of the references may be found in Boeing Document D180-19046-1.

Wherever possible the units used in this document are those adopted as the International System of Units (SI). However, to avoid the possibility of error in interpretation of data obtained from references, the units used in the original text are reproduced in this document. Often the authors used MKSA units and other units commonly used in commerce at the time the original text was developed.

It should be noted that various diagrams, graphs, or the like contained in the enclosed report are derived from portions of various copyrighted sources and constitute "fair use" of such sources. In the event extensive publication is intended, arrangements with the respective copyright owners may be advisable.

## 2.0 MANUFACTURE OF CADMIUM ELECTRODES

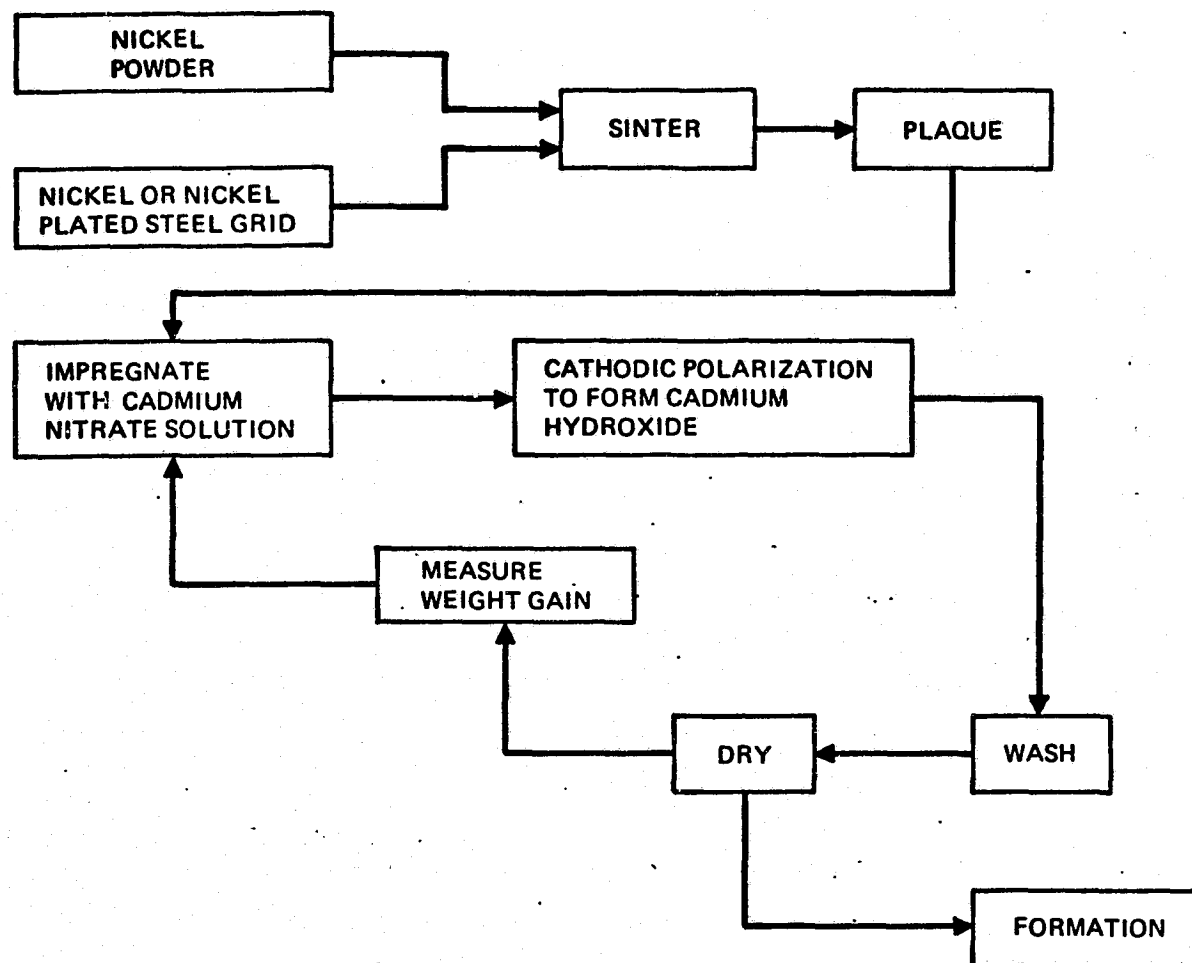
This section describes fabrication of the cadmium electrodes used in sealed nickel cadmium (NiCd) battery cells, with emphasis on manufacturing methods, research, and development since 1960. Although serious NiCd battery work started in the 1920's, development of sealed cells was not intense until the U.S space program started. Since then, much has been written to describe fabrication methods and performance of sealed nickel-cadmium batteries.

This section is divided into two major parts: (1) A detailed description of a historically significant standard method for fabricating cadmium electrodes and (2) variations available for each step in the electrode manufacturing process. The standard process, selected for historical reasons, provides a base for evaluating improvements developed by researchers and inventors.

Some discussion of additives and impurities affecting the negative plate is included in this manufacturing summary. A more complete review of additives and impurities is provided in Section 9 of this report. Also, it should be noted that some manufacturing details, being proprietary to specific manufacturers, are not included here. These details, in general, relate to solution concentrations, current density, fabrication tooling, and electrode pre-conditioning. Understanding these details is not essential to understanding of the electrode manufacturing process.

### Standard Cadmium Electrode Process

One sequence for fabricating a negative cadmium electrode is shown in Fig. 2-1. It involves sintering nickel powder on a nickel grid to form a plaque that then is impregnated with cadmium nitrate ( $\text{Cd}(\text{NO}_3)_2$ ), which by cathodic polarization is converted to cadmium hydroxide ( $\text{Cd}(\text{OH})_2$ ). After a suitable quantity of this active material has been added, the electrode is washed and dried, and assembled into a battery cell. The process details are described by Fleischer (1) in a 1956 patent disclosure. Although this process has been superseded in current aerospace practice, it does represent a historical starting point for the discussion of research into the cadmium electrode manufacturing process.



*Figure 2-1. Cadmium Electrode Manufacturing Processes*

The nickel plaque needs to have high porosity, low electrical resistance, and good mechanical strength. This combination of plaque properties is achieved by using nickel powders of low apparent density (0.45 to 0.8 gm/cc) and small particle size. The grid, a pure-nickel or nickel-plated screen, forms the core of the plaque and provides high electrical conductivity, mechanical strength, and resistance to shrinkage during sintering.

The nickel powder, fine enough to pass through a 200 mesh screen (nominal aperture 74 micrometers) is applied to the grid by a loose powder technique. One-half of the powder is poured into a steel or graphite mold, the grid is laid in, and the remaining powder is poured into the mold. The powder is scraped level to make it uniform above, below, and across the grid. A grid is 20 mesh (nominal aperture size 840 micrometers) and is made from nickel or nickel plated steel wire cloth. The 20 mesh screen assures that the grid is locked into place by bridging of the powder through the screen openings during the sintering operation.

The assembly is sintered in a furnace at  $926^{\circ}\text{C}$  ( $1700^{\circ}\text{F}$ ), having an inert or reducing atmosphere such as hydrogen or dissociated ammonia. Sintering time is 10 minutes, followed by 30 minutes for cooling.

#### Impregnation and Cathodic Polarization

Electrochemically active material is introduced into the plaque by impregnation. The plaque is submerged into an aqueous solution of cadmium nitrate, followed by cathodic polarization in a sodium or potassium hydroxide solution, and then washed and oven dried. Washing of the plates after polarization in de-ionized water removes the nitrate and hydroxyl ions. This cycle is repeated, usually three or four times, until the proper amount of active material is introduced, as measured by the gain in weight of the plate.

Maximum loading of active material into the plaque is achieved by impregnation in vacuum. Each impregnation cycle takes about 5 minutes. The impregnation solution is saturated at room temperature with respect to cadmium nitrate tetrahydrate ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), contains 3 to 4 grams per liter of nitric acid ( $\text{HNO}_3$ ), and has a specific gravity of 1.78.



Following impregnation, the electrode is cathodically polarized in a 25% potassium hydroxide solution (KOH). The impregnated plate is connected as the cathode of a nickel-plate anode in an electrolysis cell. The current density during electrolysis is 30 to 80 ma/cm<sup>2</sup> (0.2-0.5 amp/in<sup>2</sup>), with the solution at about 100°C. Cathodic polarization evolves hydrogen at the cathode, precipitates cadmium and/or cadmium hydroxide in the pores of the sintered plaque, and causes nitrate and other anions to migrate from the pores of the electrode.

Following cathodic polarization, the electrodes are washed for several hours to remove the alkali solution and residual salts. The plates are then air dried in an oven at 50° to 80°C. Completion of the drying ends the first impregnation cycle. Four impregnation cycles will usually achieve the desired weight gain. The acceptable weight gain varies widely, depending upon the cell design. Typical values range from 1.5 to 2.0 grams Cd(OH)<sub>2</sub> per cubic centimeter of plate volume. For a plate thickness of 0.075 centimeters, this corresponds to 0.1125 to 0.15 grams Cd(OH)<sub>2</sub> per square centimeter of plate area.

The last impregnation cycle of the negative electrode is followed by several charge-discharge cycles called formation. This process develops electrode capacity by exercising the active material, and aids in removing residual impurities in the plate. The plates are usually formed in an excess of KOH electrolyte and often after each charge-discharge cycle fresh electrolyte is substituted for the used solution. The number of forming cycles and current density depends on the manufacturer and the quality of the plate and loading used. Typically, there would be three forming cycles, with C/10 charge rates and substantial overcharge, followed by C/5 discharges.

Aerospace nickel-cadmium batteries need to have light weight, high reliability and long cycle-life, so extensive research has been directed at improving the cadmium electrode manufacturing process. We will now review the results of this research as it applies to each of the manufacturing steps.

#### Plaque Fabrication

Plaque fabrication has been the subject of much research. Many types of plaque have been studied searching for better consistency, uniformity, and lower cost. Table 2-1 summarizes the scope of these studies.

## TABLE 2-1-- SCOPE OF PLAQUE INVESTIGATIONS

### COMPONENTS

#### A. Nickel Powders

1. Pure nickel
  - a. Nickel carbonyl decomposition
  - b. Domestic nickel powder
2. Nickel plated powders
3. Characterizing parameters
  - a. bulk density
  - b. average particle size
  - c. surface area
  - d. particle size range

#### B. Nickel metal fibers and ribbons

#### C. Novel Approaches -- foams, corrugations, layered screens, honeycombs

#### D. Grid

1. Nickel screen
2. Nickel plated screen
3. Perforated nickel foil
4. Etched nickel foil
5. Cadmium or cadmium plated

### POWDER APPLICATION

- A. Loose powder
- B. Slurry
- C. Roll compaction
- D. Resin bonded
- E. Die pressing

### SINTERING PARAMETERS

- A. Temperature
- B. Atmosphere
- C. Time

### PLAQUE PARAMETERS

- A. Porosity
- B. Pore size distribution
- C. Surface area
- D. Electrical resistivity
- E. Thickness
- F. Strength

Casey et al (2) made plaques from a domestic nickel powder rather than from the usual nickel carbonyl powder. His finished plates, when discharged at high rates, had about 20 percent less capacity than plates fabricated from nickel carbonyl powders. Langer et al in a patent assigned to Westinghouse (3) describe a plaque composed of compacted wool fibers, which can hold more  $\text{Cd}(\text{OH})_2$  than standard powder plaques. The cadmium utilization efficiency of two electrodes made with this plaque is plotted in Fig. 2-2. Charge-discharge cycling was conducted at room temperature using a silver cathode. Discharge was considered complete when the cell voltage fell to 1.0 volt. A utilization efficiency of about 60% of theoretical was achieved.

Bidler and Fisher (4) in a NASA/Lewis Research Center sponsored study made plaques by sintering three grades of pure nickel fibers. Fig. 2-3 shows achieved plaque surface area as a function of sintering temperature. Kroger, in a NASA sponsored study (5) compared performance of plaques made from nickel fibers with standard nickel-powder plaques. Poor active-material retention and short-circuiting were found in cells made with the fiber based electrodes.

Cadmium utilization efficiency for electrodes made with experimental nickel fiber plaques is compared with that of electrodes made with nickel powder in Fig. 2-4. The electrodes were cycled to 50 percent and 120 percent depths of discharge. The 120 percent DOD implies a reversal of the potential of the test electrodes. The control electrodes having nickel powder plaques consistently showed better active material utilization. The observed utilization was corrected to account for the loss of active material from the electrodes. Assuming that the active material loss is evenly distributed over the test cycles, the reduction in theoretical capacity from the start to the end of the test results in the corrected utilization line labeled "COR" in Fig. 2-4.

Schaer et al (6) studied plaques of corrugated nickel foil in a honeycomb structure. The stacked corrugated nickel foils were heat bonded at  $1940^\circ\text{F}$  and then sliced to the required thickness. (Fig. 2-5). Preliminary evaluation of electrodes made from these plaques indicate capacities comparable to conventional sintered powder electrodes. Extensive cycle testing was not conducted. Other attempts have also been tried for making plaques of controlled geometry by novel methods such as sandwiching many screen layers or use of foaming techniques; however, porosity was low, pore size was large, and little or no cycle testing was done.

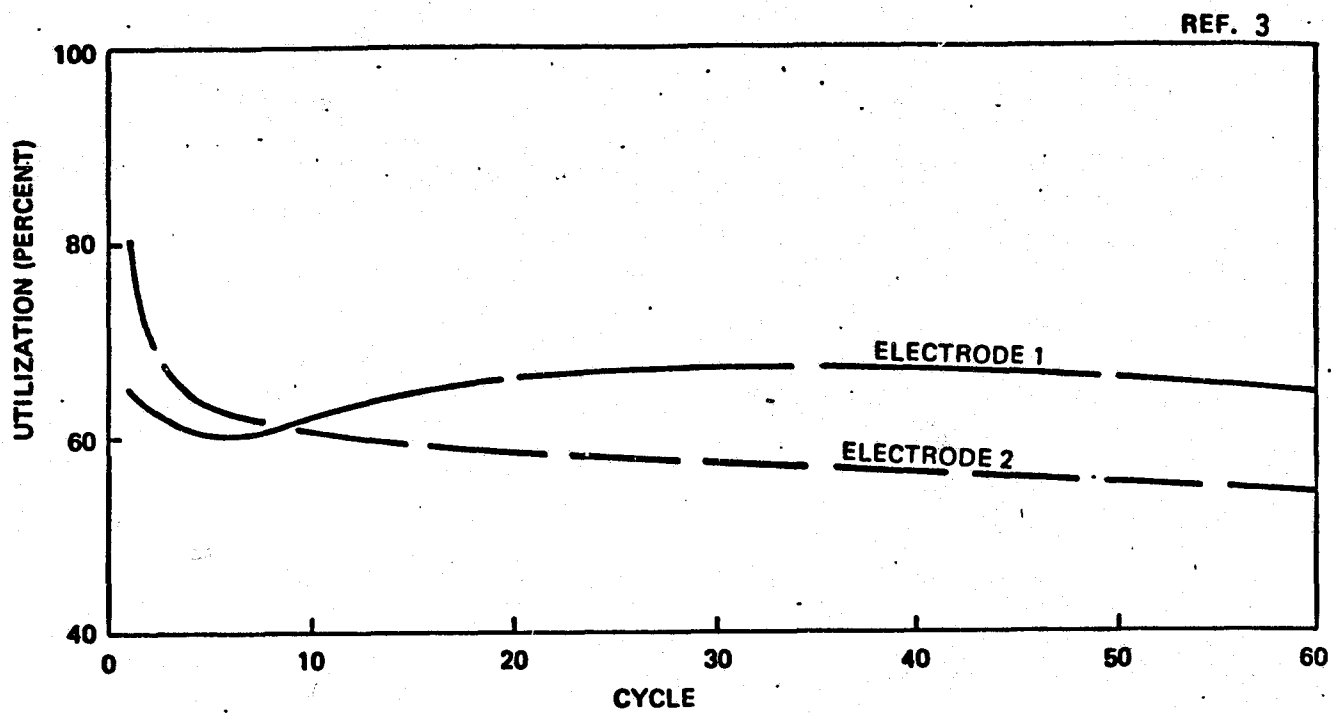


Figure 2-2. Cadmium Utilization Efficiency of Cadmium Plated Steel-Fiber Plaque, 100% DOD, 20°C

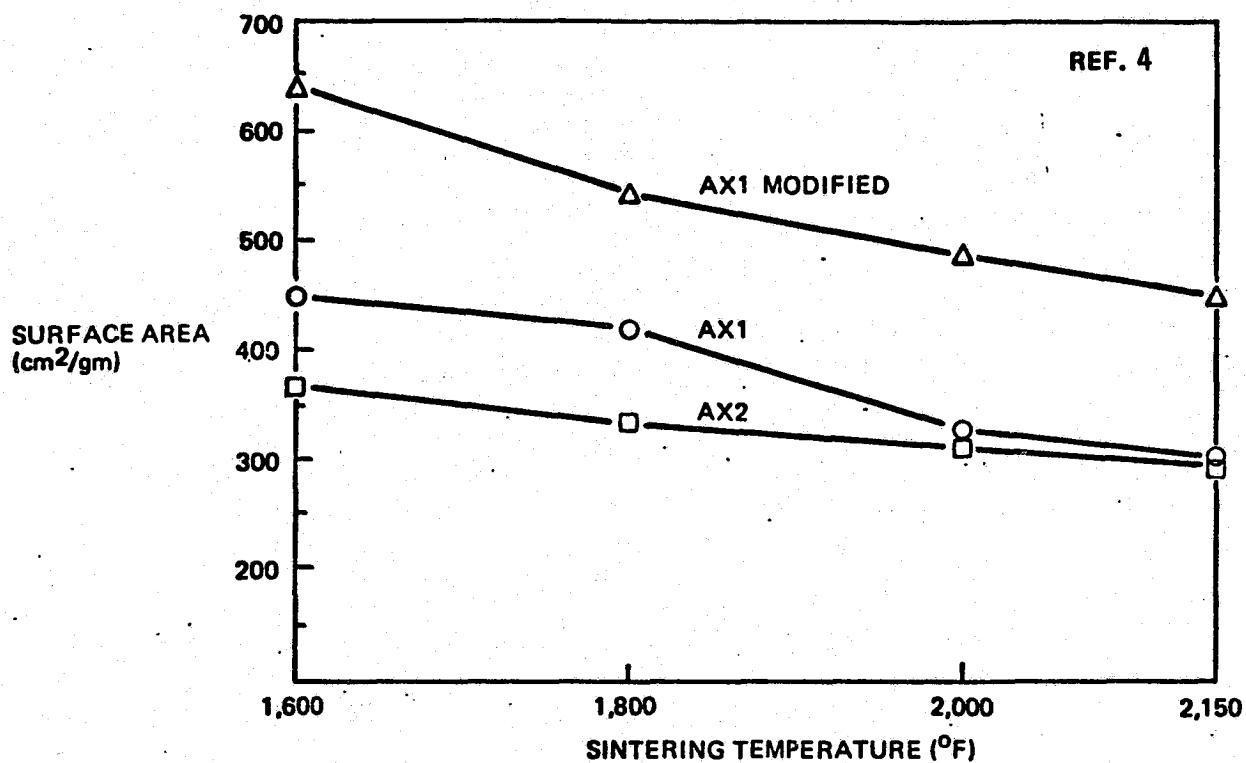


Figure 2-3. Internal Surface Area Delivered in Modified Nickel Fiber Plaques

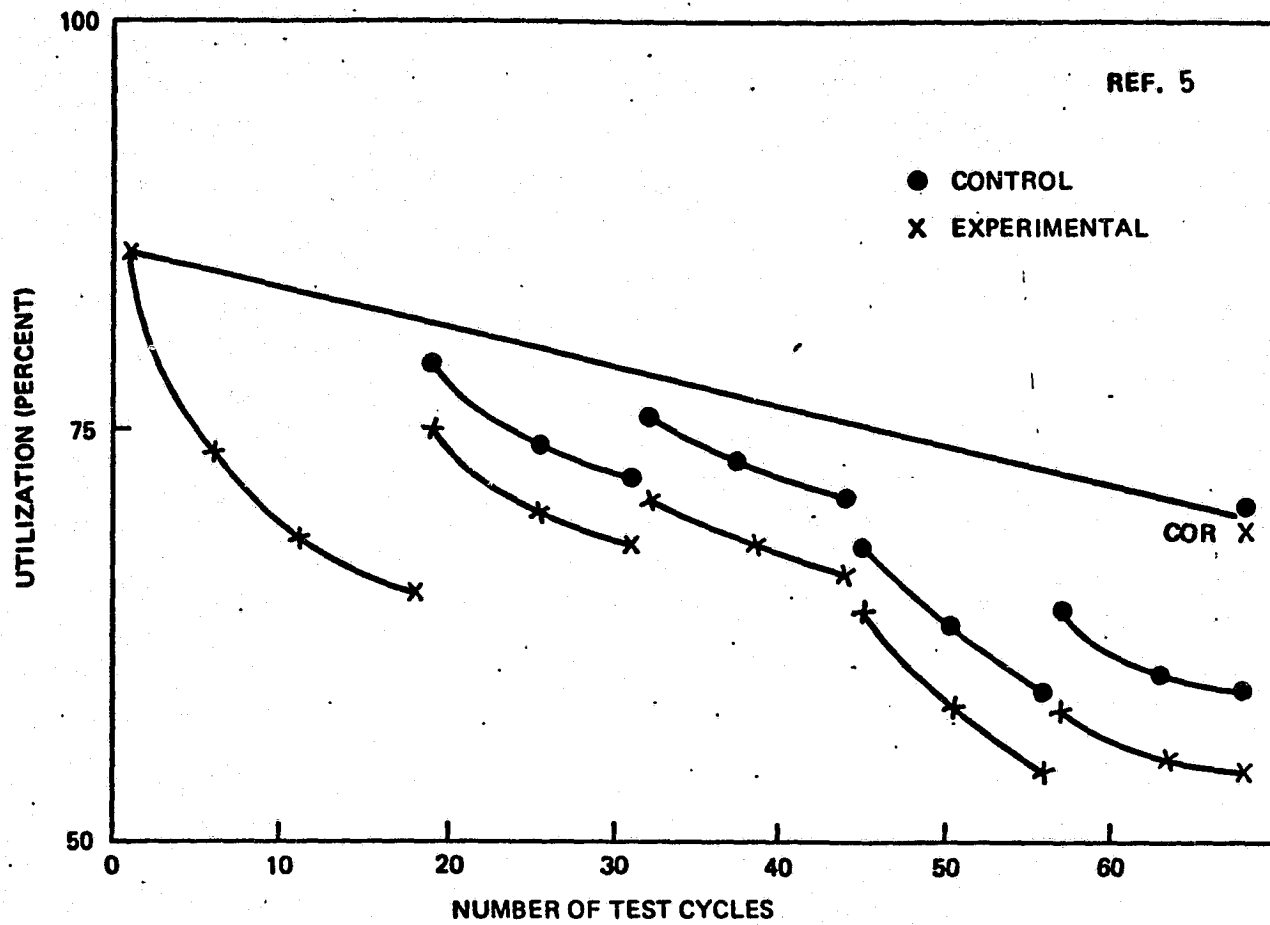
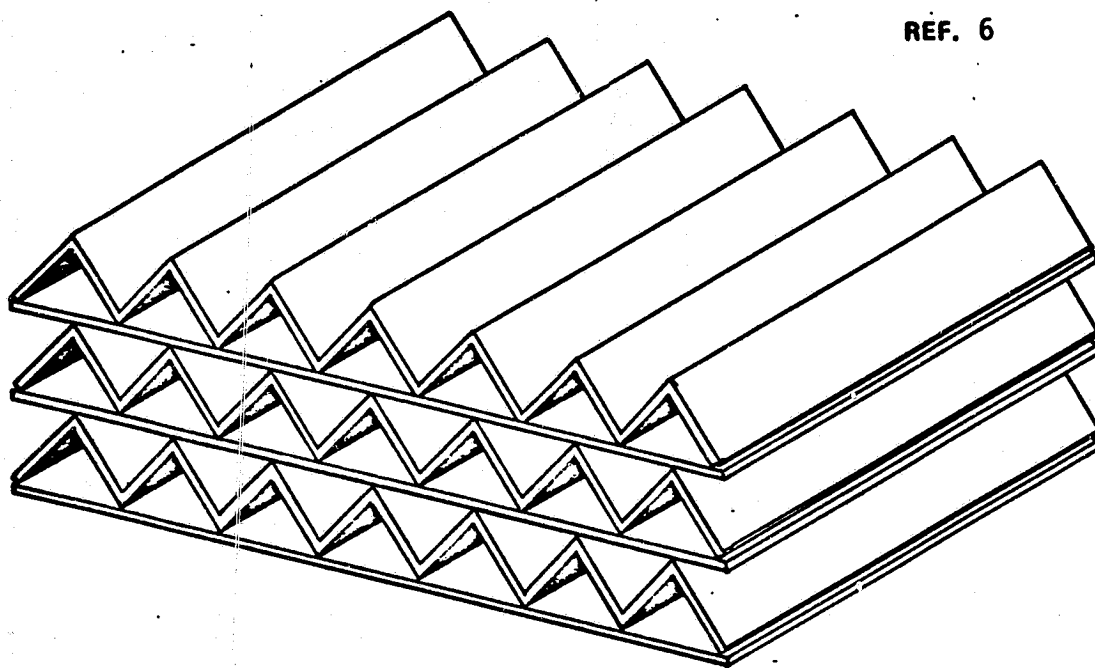


Figure 2-4. Utilization Factors Achieved With Nickel-Fiber Plaques



**Figure 2-5. Layered Honeycomb Structure (Not to Scale)**



One novel approach that does have good promise theoretically is a plaque formed of felted and sintered nickel microribbons. Such ribbons can be made easily and economically by an electroforming process (7). The key point of this concept is that a thin metal ribbon substructure can provide greater surface area and porosity than a powder-based structure. Westinghouse has developed a plaque for a proprietary nickel electrode based on this principle. No applications to the cadmium electrode are known, however.

The most common method of plaque manufacture involves sintering a nickel powder onto a grid. In a NASA/Goddard sponsored study, Tyco Laboratories investigated some plaque fabrication methods currently used in the manufacture of aerospace cells (8). They observed that the objectives of plaque manufacture are generally 80 percent porosity, good mechanical strength, good electrical conductivity, and uniform thickness and pore size distribution. They report that virtually all the nickel powders for aerospace plaques are derived from the decomposition of nickel carbonyl ( $\text{NiCO}_4$ ).

The relation between sintering time and porosity for various sintering temperatures was studied by Tracey (9) and is shown in Fig. 2-6. The pore sizes in the sintered plaque should be consistent with the required plate performance. Large pores result in low surface area and high plate polarization during charge and discharge. Small pores constrict electrolyte flow within the plate. Best overall performance is obtained when 60 percent of the total pore volume is in pores whose diameters are in the range of four to fifteen micrometers.

Tarasov et al, in a Russian publication (10), describe plaque fabrication using a paste of nickel carbonyl powder (1kg of specific gravity 0.49) and carboxymethyl cellulose (1kg of 4 percent solution containing 44 gm glycerol) applied to both sides of a perforated nickel plate. The optimum sintering temperature was  $1000^{\circ}\text{C}$ , held for 15 minutes. Seiger, in a NASA-sponsored study (11), investigated plaque fabrication using a slurry or paste technique with particular emphasis on obtaining a uniform and blemish-free plaque with predictable performance, suitable for large aerospace cells. Kuniake et al, in a recent Japanese paper (12), indicate that a foamed slurry results, after sintering, in a plaque having a porosity higher (75 to 85 percent) than can be obtained with other techniques. In a recent patent, Papat and Rubin (13) indicate that a cadmium or cadmium-plated grid facilitates low

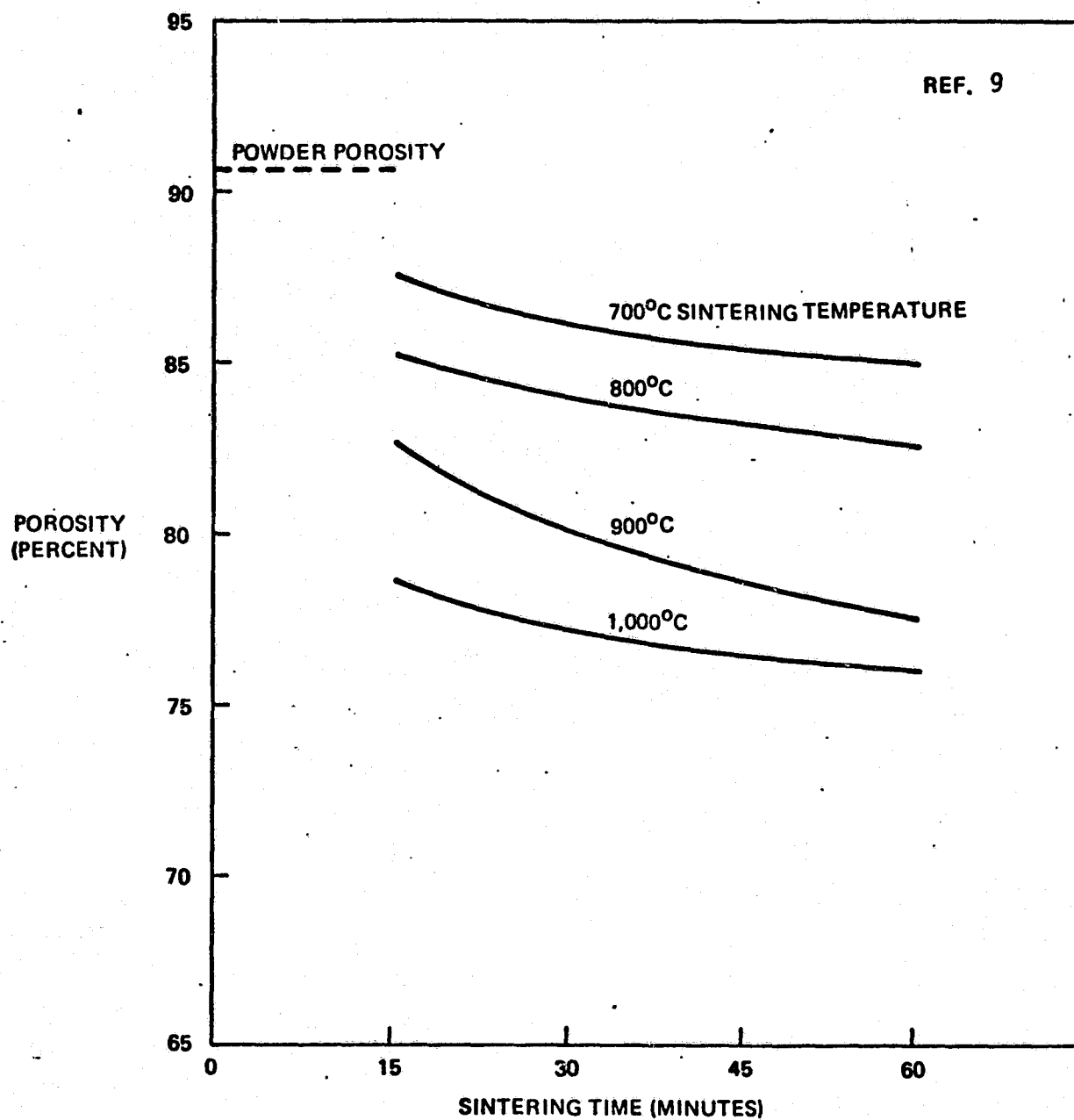


Figure 2-6. High Porosity Results From Low Sintering Temperatures

low temperature ( $-40^{\circ}\text{C}$ ) charging of negative cadmium electrodes. Menard and Luksha (14), in a technical paper describe a nickel plaque made by isostatic compression of nickel powder in a suitable mold.

There are two recent advances in plaque making that are of great significance. The one is the plaque developed by Bell Telephone Laboratories, having high strength and a very narrow, well-controlled pore size distribution.\* Test data are not publicly available, however. The second development is by Seiger et al under an Air Force contract (15). The significant finding in this work was that plaque strength could be greatly increased by introducing an oxidizing zone prior to the reduction zone in the sintering process. This is effective partly because it gets rid of adsorbed gases, and partly because freshly reduced nickel surfaces are very active. Such strong sinters exhibit little necking-down between fused nickel particles. Having developed a technique for making strong, well-controlled plaques, it is then possible to increase the porosity and obtain either higher loading, greater void volume, or a suitable compromise. The cadmium electrodes developed in this work had sinter porosities of 89 to 90 percent.

### Impregnation

Besides being time consuming and expensive, the impregnation process influences the performance of the negative plate. Because of its importance, the impregnation process has been extensively studied. Falk, in a patent (16) describes impregnation by immersion in a solution of cadmium nitrate and cadmium formate or acetate, followed by heating to decompose the impregnated salts. Beauchamp, in a technical paper and patent (17, 18) describes a one-step impregnation method in which a solution of  $\text{Cd}(\text{OH})_2$  and  $\text{NaNO}_2$  is held at its boiling point. Operating at  $77.5 \text{ ma/cm}^2$ , a plate loading of  $1.75 \text{ gm Cd}(\text{OH})_2$  per cubic centimeter of plate volume was obtained in 15 minutes.

Jost, in a patent (19) describes a satisfactory plate made by spreading cadmium nitrate powder over a sintered plaque, and melting the powder to impregnate the plaque, followed by conversion to the hydroxide. Korman, in a patent (20) describes a novel impregnation solution in which the ratio of water to cadmium is held between 1.3 and 3.0. The solutions are prepared by removing water from molten  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . Miller et al, in a NASA sponsored study of impregnation variables (21) indicate that use of a low specific-gravity solution of  $\text{Cd}(\text{NO}_3)_2$  with long impregnation and polarization times, results in maximum weight gain with good electrical

\* Private communications, D. Maurer

capacity and physical characteristics. Gamaskin and Pozin, in a Russian paper (22, 23) say that impregnation using a  $\text{CdCl}_2$  solution containing nitrate ions under cathodic polarization reduces the time needed for satisfactory weight gain, and minimizes corrosion of the nickel sinter.

Fleischer's method of fabricating plaques was compared with the chemical conversion method in an extensive study by Tyco Laboratories (24) for NASA/Goddard. The objective of the study was to develop uniform and predictable materials for aerospace cells. The achieved weight gains and capacities are shown in Fig. 2-7. The chemical conversion technique involved drying for 2 to 3 hours at  $80^\circ\text{C}$  after vacuum impregnation, followed by immersion in hot potassium hydroxide (KOH) without cathodic polarization. Tyco concluded that of the two methods, the chemical conversion process provides more uniform and reproducible materials.

In a patent assigned to SAFT, Pinard (25) recommends heating the impregnated  $\text{Cd}(\text{OH})_2$  plate to  $200^\circ$  to  $500^\circ\text{C}$  to convert both the  $\text{Cd}(\text{OH})_2$  and a small amount of  $\text{Ni}(\text{OH})_2$  to their respective oxides. The  $\text{CdO}$  is rehydrated by immersion in an aqueous solution of sodium or potassium hydroxide at  $80^\circ\text{C}$  for one to two hours. This treatment converts the cadmium oxide to the hydroxide without affecting the nickel oxide. The resultant negative electrode is said to have less parasitic positive active material and more porosity. Pickett, in a recent AFAPL report (26) indicates that plate loadings in the range of 2.1 to 2.3 gm  $\text{Cd}(\text{OH})_2$  per cubic centimeter can be achieved with an alternating-current-pulse electrochemical impregnation technique. His plates show promise, and evaluation is continuing.

Pozin et al, in a Russian paper published in 1973 (27) indicate that higher plate loading is obtained from mixed cadmium salt solutions, e.g.,  $\text{CdCl}_2 + \text{Cd}(\text{NO}_3)_2$ , if the  $\text{Cd}(\text{NO}_3)_2$  concentration is kept low. Romanov and Viktorova, in another recent Russian paper (28) state that a significant reduction in impregnation time is achieved if an organic cadmium salt solution (e.g.,  $(\text{Cd}(\text{OAc})_2)$  is used and followed by thermal decomposition. This approach eliminates conversion to the hydroxide in  $\text{NaOH}$  or  $\text{KOH}$  solutions as well as the washing and drying steps. However, four to five cycles of impregnation-decomposition are needed to achieve a proper plate loading of 1.5-1.7 gm/cc. Kuniaki et al, in a Japanese paper (29) report that addition of a nonionic surfactant to the impregnating solution improved overall cadmium loading when compared to conventional impregnation without the surfactant.

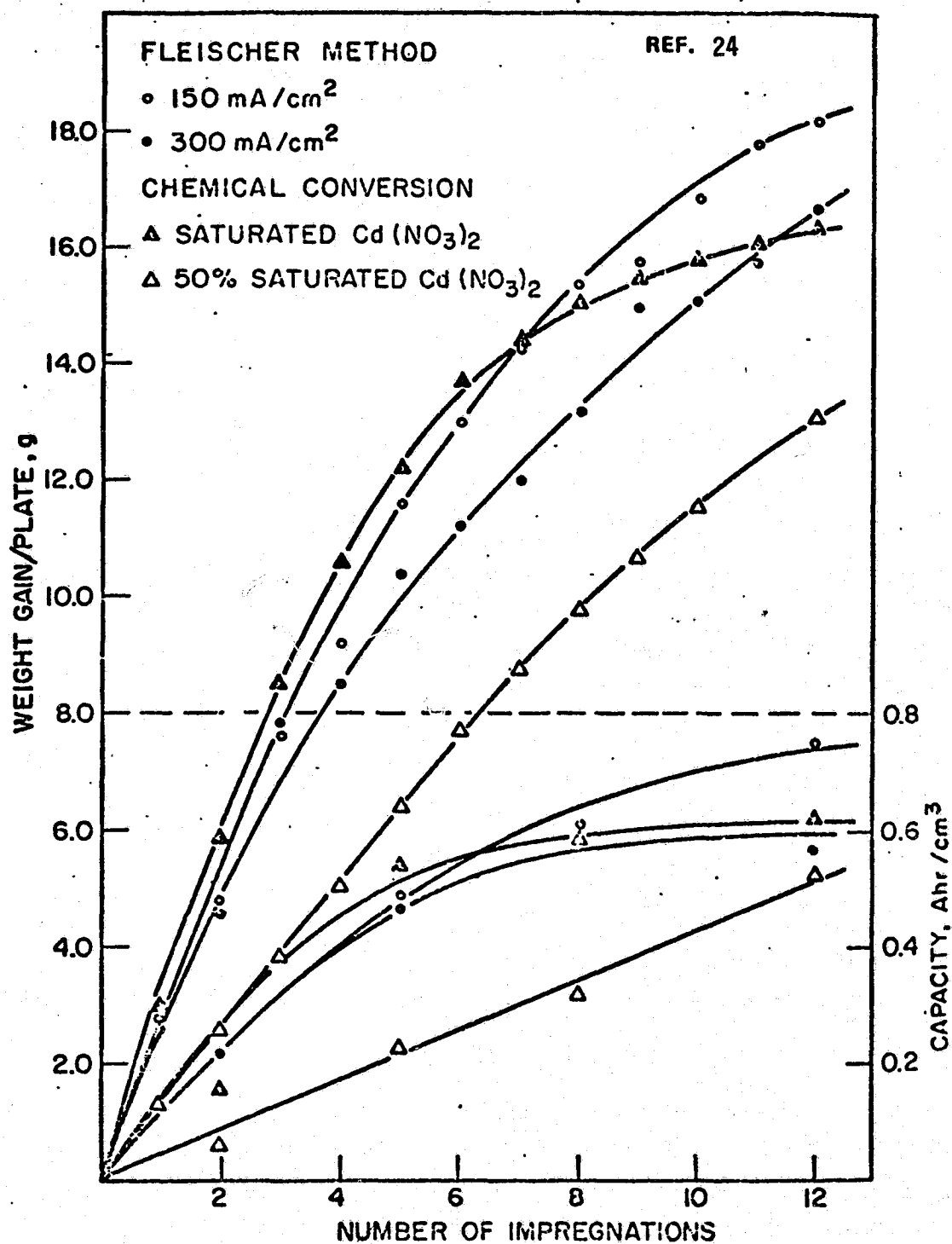


Figure 2-7. Weight Gain and Capacity for Fleischer and Chemical Conversion Methods for Making Negative Plates

Nervik, in a patent assigned to ESB Inc. (30) proposes that fully impregnated plaques which have been converted to  $\text{Cd}(\text{OH})_2$  be heated to  $350^\circ$  to  $900^\circ\text{C}$  to decompose residual nitrates. The plates are then soaked in hot alkaline solution to convert  $\text{CdO}$  to  $\text{Cd}(\text{OH})_2$  and washed and dried. He claims that this process minimizes plaque corrosion by not exposing the plaque to a hot nitrate solution, thus reducing residual nitrate to less than 0.03 percent. Fukuda, in a Japanese patent (31) recommends drying at  $40^\circ$  to  $60^\circ\text{C}$  in an inert atmosphere to avoid carbonate contamination.

### Additives

The use of additives during plate fabrication has been controversial among researchers. In an early study, Fleischer stated that indium added to the negative active material acts as an expander to improve battery performance (32). On the other hand, Christy, in an NAD, Crane report (33) states that a cobalt additive suppresses both charge and discharge voltage, and cells having cobalt added deliver significantly less capacity. Another study reports the opposite, that cobalt increased capacity of the cadmium electrode (34). Rampel, in a patent assigned to General Electric (35) claims that impregnating the cadmium electrode with metallic silver catalyzes oxygen recombination on overcharge and avoids excessive cell internal pressure. Effects of additives and impurities are discussed in detail in a later section.

### Plated Cadmium Electrodes

One way of making a negative cadmium electrode is to plate the cadmium directly on a grid. This technique is used for some commercial cells, but is not generally used for aerospace cells. It is an option which could be used in some cell designs.

Mueller, in a patent assigned to Union Carbide Corp. (36), describes a cadmium electrode electroplated on a 40 by 40 nickel mesh suspended between cadmium rods in a 50 weight percent  $\text{Cd}(\text{NO}_3)_2$  aqueous solution. The mesh is plated at  $20^\circ\text{C}$  with about  $180 \text{ ma/cm}^2$ , and the solution pH is maintained at 1 to 1.5 with  $\text{HNO}_3$ . The deposited  $\text{Cd}(\text{OH})_2$  is electrolytically converted to Cd in a 30 weight percent aqueous KOH solution using the same current density. The spongy Cd deposit is compressed between smooth nickel rollers to a desired thickness. Electrodes produced in this manner are claimed to charge better and suffer less self-discharge when compared with conventional electrodes.

Henderson and Ladan, in a 1967 patent (37) electroplate Cd on nickel foil from an aqueous  $\text{CdCl}_2$  solution at pH 5 to 6 using a current density up to  $20 \text{ ma/cm}^2$ . Cadmium sulfate solutions containing a little arsenic trioxide and sodium sulfate or ammonium sulfate are described as excellent for cadmium plating in a patent assigned to Joseph Lucas Ltd. (38). Current densities up to  $300 \text{ ma/cm}^2$  could be used.

Luksha, in a NASA/JPL sponsored study aimed at producing "non-gassing" electrodes (39) electrodeposited cadmium on porous silver plaques. Pickett, in a patent application filed in 1973 (40) described electroplating cadmium into a porous nickel plaque in an aqueous  $(\text{Cd}(\text{NO}_3)_2)$  bath maintained at pH 3 to 5 and  $95^\circ$  to  $110^\circ$  at a current density of 180 to  $250 \text{ ma/cm}^2$ .

#### Cadmium Plate Fabrication

Cadmium electrodes are made with processes that differ significantly from the standard process described earlier, and by processes that merely have simple variations in one or more of the steps. However, each change represents innovations which may benefit a specific cell design.

Peters, in a patent (41) assigned to Accumulatoren-Fabrik A.G. (now Varta) indicated that improved oxygen consumption is obtained in sealed nickel-cadmium cells if the cadmium electrodes are compressed from mixed Cd and Ni powders in the ratio 1:1 to 1:4 by volume. Stark, in a patent assigned to Union Carbide Corp. (42) describes a cadmium electrode made by flame spraying a 2:1 to 20:1 mixture of molten Cd:Al on a suitable substrate and removing the aluminum in a bath containing  $\text{CdSO}_4$ , HF, and  $\text{H}_2\text{O}$ . The resulting electrode had a passivity current density of  $425 \text{ ma/cm}^2$ .

Another innovative cadmium electrode is described in a patent assigned to ESB Inc. by Smith (43). In Smith's process, CdO is suspended in a thermoplastic resin with a soluble pore former such as polyethylene oxide. The mixture is passed between rollers to produce a coil or flat sheet. A similar sheet is made from nickel powder. Two cadmium sheets, separated by a nickel sheet, are then pressed between rollers at  $150^\circ\text{C}$  and the soluble pore former is leached out with warm water. A Western Electric Co. patent application (44) describes melting cadmium foil into a porous nickel plaque in a reducing atmosphere.



Lauzas, in a 1967 patent (45), assigned to Union Carbide Corp., describes blending graphite and  $\text{CdI}_2$ , compressing the mixture on a nickel mesh screen, followed by cathodic reduction in KI solution. The resulting electrode had a limiting current density of  $190 \text{ ma/cm}^2$ . SAFT, in a 1967 French patent (46) describes impregnating porous graphite fiber felt in  $\text{Cd}(\text{NO}_3)_2$  solution followed by conversion to  $\text{Cd}(\text{OH})_2$  in a soda solution. This process yielded electrodes with 50 percent porosity. McCallum et al, in a NASA sponsored study (47), claims that the preferred method for obtaining a large surface area is to impregnate into porous nickel plaque fused cadmium nitrate hydrate, followed by a hot soak in KOH solution. Kelly and Przybyla, in a 1969 Canadian patent (48) make cadmium electrodes by mixing Cd powder with a suitable subliming agent, and heating under pressure to remove the subliming agent to form a 60 percent porous, open three-dimensional cadmium network. Shepherd and Langelan (49) prepared cadmium electrodes having high surface area and controlled porosity by electrolytic reduction of cadmium oxide under controlled physical pressure. These electrodes are said to provide excellent high-rate discharge performance and high coulombic efficiency.

Holleck et al, in a NASA/JPL sponsored study seeking high hydrogen overvoltage (50), investigated silver-sinter based Cd electrodes, Teflon bonded Cd electrodes, electro-deposited Cd sponge, and Cd sinter electrodes. They found that hydrogen evolution potentials on pure Cd structures were 50 to 70 mV more cathodic than on those containing silver. Yamamoto et al, in a 1937 U.S. patent assigned to Matsushita Industries (51), describe the fabrication of a cadmium electrode composed of a mixture of nickel or carbon with cadmium within an alkali-resistant, electro-chemically inert resin fiber. Gottlieb, in a 1968 patent assigned to Bell Telephone Laboratories (52) recommends coating the sintered nickel plaque with mercury by immersion in a seven percent mercuric chloride solution for 30 minutes prior to impregnation. This process is said to result in hydrogen overvoltages 0.3 volts higher than similar electrodes without the treatment.

Carr, in a 1972 paper (53), describes the fabrication of a lightweight sponge cadmium electrode by pressing a mixture of  $\text{CdO}$ , binders, expander, and conductive additives onto both sides of an expanded nickel mesh. Compared to cadmium electrodes manufactured with the standard process, the energy density of this sponge electrode is said to be 70 percent greater, active material utilization efficiency

about 10 percent greater (80 percent vs 70 percent) and nominal loading more than double (3.23 gm/cc vs 1.59 gm/cc).

In 1975 Puglisi and Ralph developed for the USAF a specification for fabricating electrodes for lightweight nickel-cadmium cells (15) . Table 2-2 summarizes the steps in manufacturing methods for cadmium electrodes, and the controls used. This manufacturing process probably represents the best technology available in mid-1976 for manufacturing cadmium electrodes for long-life lightweight aerospace cells.

TABLE 2-2    USAF LIGHTWEIGHT AEROSPACE CADMIUM ELECTRODE MANUFACTURING PROCESS

GRID

Pure nickel substrate nickel alloy 270 or 200  
 0.0030 + 0.005 in. thick  
 0.045 inch holes on 0.066 inch centers

NICKEL POWDER

Inco type 255  
 (nickel carbonyl powder)

BINDER

Union Carbide WSR-205 Polyox

PORE FORMER

Baker & Adamson purified grade Oxamide

SINTERING

3-zone furnace, 750°C, 900°C, 950°C

ELECTROCHEMICAL IMPREGNATION

1.8-2.0 Molar aqueous  $\text{Cd}(\text{NO}_3)_2$   
 1.4 amp/in<sup>2</sup> current density  
 18 min impregnation time  
 95°-105°C solution temperature  
 99.5%-99.9% cadmium anodes  
 Solution p<sup>H</sup> 3.5-4.0 prior to deposition

WASH

Prior to washing, scrub surface to remove excess surface deposit. Deionized water to negative phenolphthalein test.

SLURRY FORMULATION

<u>Component</u>	<u>Relative Amount</u>
Polyox	165
Water	2700
Methanol	600
Nickel Powder	3234
Oxamide	1478
Add water to lower viscosity to 350 Kcp	

PLAQUE

0.0325 ± 0.0010 in. thick  
 Integral tab

CATHODIC POLARIZATION

0.285 amp/in<sup>2</sup> current density  
 15% KOH solution  
 80°C solution temperature  
 2 hr. polarization time  
 Nickel alloy 270 anode

DRY

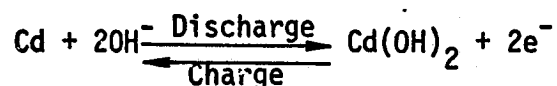
30° - 110°C air dry

### 3.0 ELECTROCHEMICAL REACTIONS

This section gives a brief summary of the reaction processes of the cadmium electrode, including cell potential, intermediates that are important to the reactions, passivation during discharge, charge behavior, electrolyte effects, and thermal effects. This provides some of the background needed to understand how the electrode works, and refers to sources where more detailed information can be obtained. Reactions associated with oxygen recombination and hydrogen evolution are postponed for inclusion in those sections.

#### Electrode Potential

The overall reaction at the cadmium negative electrode is



The theoretical equilibrium potential (54) is  $-0.809\text{V}^*$  at  $25^\circ\text{C}$  in zero percent KOH, when measured from a standard hydrogen electrode (S.H.E.). At 30 percent KOH concentration, the equilibrium potential is  $-0.851$  versus S.H.E. (55) or  $-0.899$  versus Hg-HgO (56). Actual measured values are within 10 mV of those predicted by theory. The isothermal temperature coefficient of the reaction is  $-1.014 \text{ mV}/^\circ\text{K}$  (54). Voltage-temperature-potential data provided in Reference (55) are inconsistent with data in Reference (54) and with calculations based on the temperature coefficient. It is interesting that the nickel positive and cadmium negative potentials partially compensate for changing electrolyte concentration, although the cadmium negative electrode is more sensitive, changing 26 mV between 20 percent and 30 percent KOH concentration (55).

Many investigators working with the cadmium electrode prefer the HgO-Hg reference electrode, for it eliminates liquid junction errors. Reference (57) tells how to construct this reference electrode, and reports potentials of the cadmium electrode versus temperature and electrolyte concentration. Nickel oxide electrodes (58, 59) and zinc electrodes (28, 34) have also been used as references.

- \* The reduction potential is the convention that is followed here. Sometimes the oxidation potential is reported, and is indicated by the opposite sign.

The potential of the nickel positive electrode changes significantly with state-of-charge. The cadmium negative electrode potential, on the other hand, changes little, being quite flat for both charge and discharge. Thus, under typical conditions, most of the potential change with state-of-charge is caused by phenomena at the nickel positive electrode, rather than at the cadmium negative electrode.

Overpotential at the cadmium negative electrode is relatively small, being around 60 mV during charge and 15 mV during discharge at C/2 rate, plus small overshoots at the beginning of both charge and discharge (56). By contrast, the total overpotential at the nickel positive electrode is about twice that at the cadmium electrode. One reason for this difference is that the nickel-electrode reaction requires water absorption during discharge and water release during charge, resulting in significant concentration polarization, whereas no water is exchanged in the reaction at the cadmium negative electrode. Both electrodes have high exchange currents and thus have good high-rate capability (60).

Carbonate ions are a common impurity in nickel cadmium cells, lowering the equilibrium potential (55). The nickel positive electrode is affected about twice as much as is the cadmium negative electrode. A peculiar feature common to both electrodes is that the theoretical voltage change attributable to carbonate addition goes through a maximum at about two percent carbonate. With 30.3 percent KOH at 20°C, the negative-electrode potential is -0.851 volts vs S.H.E. with zero percent carbonate, and -0.801 volts with two percent carbonate (55).

In evaluating the potential changes caused by carbonate, it is important to distinguish between carbonate that is in the cell initially and carbonate coming from separator decomposition after the cell is sealed (61, p.203). The latter is produced at the expense of hydroxide ions (61, p.174). Lowering the hydroxide ion concentration raises the negative potential, thus offsetting to some extent the effects of carbonate produced. Other effects of carbonate ions are discussed in the section on impurities.

Carbonates must be considered also as additional electrodes in the nickel cadmium cell, producing a mixed potential. At the negative electrode, in addition to the cadmium/cadmium hydroxide couple, there will be a cadmium/cadmium carbonate couple (55) which in the following reaction produces the voltage,  $E_c$ :

$$\text{CdCO}_3 + 2\text{e}^- = \text{Cd} + \text{CO}_3^{-2}$$

$$E_c = -0.74 - \frac{1.985 \times 10^{-4}}{2} T \log a_{\text{CO}_3^{-2}}$$

where  $a_{\text{CO}_3^{-2}}$  is the activity of carbonate ions.

The rest potential of these two mixed negative-electrode couples will be intermediate between their separate rest potentials and will be closest to that of the couple with the higher exchange current density, typically the cadmium/cadmium hydroxide couple.

### Soluble Intermediates

The soluble intermediates generated in the transitions between cadmium and cadmium hydroxide have not been adequately determined. Metallic cadmium has essentially zero solubility as  $\text{Cd}^{+2}$  in KOH solutions (62). However, cadmium does form hydroxide complexes which are slightly soluble. It is this solubility that makes the electrode function, but as a result of it, the electrode undergoes morphological changes that reduce cycle life of cells.

Cadmium hydroxide solubility has been measured by many investigators (63, 64, 65, 66, 67, and 68). This solubility is small, being only about 15 milligrams per liter at 20°C with six normal KOH. Solubility increases with temperature, concentration, and carbonate ion content. Harivel's transient data on solubility (63) shows that at 6N and 20°C the time constant (63% complete) is about 1½ hours.

Attempts to identify the species in the electrolyte have not produced clear answers. One important discovery was that after passivation by the underlayer and the onset of oxygen evolution, the radicals  $\text{O}_2^-$  (superoxide) and  $\text{O}_3^-$  (ozonide) appear (69). It is hypothesized that these radicals are derived from the underlayer, perhaps  $\text{CdO}$ , during oxygen evolution, while the underlayer dissolves into a soluble complex which then forms cadmium hydroxide. Precisely what all the species and intermediate reactions are is not known. One unidentified species was found in solution by ESR analysis (69).

The predominant soluble complex is generally thought to be either  $\text{Cd}(\text{OH})_3^-$  or  $\text{Cd}(\text{OH})_4^{=}$ . Ryans, et al., using a colorimetric method based on the measurement of fluorescence, tested the solubility of cadmium hydroxide with changing hydroxide

ion concentration (70). They found that  $\text{Cd}(\text{OH})_4^{=}$  predominated at high electrolyte concentrations, and  $\text{CdOH}^+$  predominated at low concentrations. They also found  $\text{Cd}(\text{OH})_3^-$ , soluble  $\text{Cd}(\text{OH})_2$ , and very little  $\text{Cd}^{2+}$ .

In tests with cadmium amalgams using a sitting-drop electrode and a hanging drop electrode, Armstrong, et al., obtained  $\text{Cd}(\text{OH})_4^{=}$  early in anodization before passivation occurred (71). Further proof that there is a dissolved intermediate species was produced by Okinaka (72) who used a ring-disk method. He thought that the intermediate is  $\text{Cd}(\text{OH})_3^-$ , agreeing with the arguments of Milner and Thomas (56).

Gilman and Sangermano collected absorbed cadmium ions on a platinum-catalyzed oxygen electrode in 1N KOH (73) even though Ryans, et al., had shown that there are very few free cadmium ions in solutions having such concentration (70). Visco and Sonner, using a polarographic technique, concluded that  $\text{Cd}(\text{OH})_3^-$  is the principle soluble species (68).

Hampson and Latham, in testing cadmium electrodes in NaOH using ac impedance and double pulse galvanostatic techniques, found that the charge transfer is very rapid (60). They also determined that the active area of the surface is reduced with time during anodization, and suggested that their observed impedance increase is caused by blockage.

Armstrong, et al., in testing sintered-plate cadmium electrodes, found no electrochemical differences between them and smooth cadmium plated electrodes (74). The dissolved species they obtained during the initial part of the anodization was  $\text{Cd}(\text{OH})_4^{=}$ , in agreement with their previous work (71).

MacArthur, in experiments in which mass transfer was by linear diffusion only (75), found that the anodization of cadmium occurs by dissolution, followed by a homogenous reaction in competition with precipitation. His KOH concentration was only 3.3 molal, however.

In summary, the experiments on soluble intermediates provide a mosaic of results with many important pieces missing. Additional work in this field will be needed to clear up the picture. The key experiments are not easy to define, especially those involving the detection of highly unstable intermediates.



### Reaction Intermediates--The CdO Film Question

The question of whether or not passivation is caused by a film of CdO is not entirely academic, for a better understanding of how the electrode works will help to improve the electrode efficiency. If a CdO film is found to be responsible, then research might emphasize more the chemical aspects, including detailed reactions and effects of impurities. If passivation is caused by  $\text{Cd}(\text{OH})_2$  blocking the underlying cadmium metal, then more emphasis would be expected on optimization of plaque structure and on impregnation methods that give the desired geometry of active material.

Much effort has gone into studying the detailed electrochemical reactions at the cadmium-electrode. However, the intermediate reactions for equation (3-1) are still obscure, and our knowledge of the mechanisms for the formation of anodic films on solid cadmium is inadequate. The electrode does passivate on oxidation (discharge) due to some type of film formation in which a soluble intermediate is clearly involved, with solid state reactions also occurring. The main questions are: (1) What is the mechanism by which cadmium metal ceases to be anodically oxidizable after a period of active oxidation? Possibly CdO forms between the metallic cadmium and the cadmium hydroxide. (2) What are the important soluble intermediates? Answers to these questions, especially the first one, are important, for if the onset of passivation can be delayed, then the negative plates can be more efficiently utilized. The literature gives conflicting answers to both questions.

The idea that a cadmium oxide film is formed, possibly as a precursor of the dissolved species, occurred in 1900 to Edison who suggested the existence of  $\text{Cd}_2\text{O}$  film (British Pat. 20960). The CdO film was postulated in 1928 (76). Cadmium suboxide  $\text{Cd}_2\text{O}$  is green, and this color has not been observed on cadmium electrodes, whereas the brown color of CdO has occasionally been observed. No recent mention has been made of either  $\text{Cd}_2\text{O}$  on electrodes nor of the other oxides- $\text{Cd}_4\text{O}$  or cadmium peroxide which has a composition ranging from  $\text{Cd}_5\text{O}_8$  to  $\text{Cd}_3\text{O}_5$  (9, 77).

If a CdO layer does exist, it appears to be limited to only a few monolayers. The following are the results from major investigations on the existence of a CdO film:

1. Lake and Casey, based on the analysis of overpotential decay curves, proposed a model of an oxidizing cadmium electrode with a CdO layer covering the cadmium metal (78, 79, 80), the model consisting of cadmium metal, a layer of CdO, a highly polarized inner double-layer in which the reaction  $\text{OH}^- \rightarrow \text{O}^- + \text{H}^+$  takes place, and then the Helmholtz double layer next to the free electrolyte. Their evidence indicates that the CdO film converts to  $\text{Cd}(\text{OH})_2$  during open circuit.
2. Breiter and Vetter studied smooth cadmium electrodes at constant potential (81), the investigation being aided by electron microscopy, infra-red spectroscopy, and x-ray diffraction. They found that the total amount of hydroxide decreases with potential, and that at overpotentials of over 0.1 volt the amount of hydroxide is smaller than what would correspond to 100 percent efficiency of cadmium hydroxide formation. This deficit is attributed to the simultaneous formation of amorphous CdO. X-ray diffraction patterns of the films did show traces of CdO lines, so they concluded that the oxide must be present in a largely amorphous form, and that the nature and growth of the amorphous CdO is controlled by a solid state transport process. They also concluded that thick films of CdO, when anodically formed, convert into beta-type cadmium hydroxide only very slowly.
3. Croft, using cyclic voltammetry and constant potential, found that the rate of oxidation was a monotonically increasing function of the overpotential, and after a sufficient time has elapsed, the rate of oxidation follows a parabolic growth law (82). His results did not require postulation of a cadmium oxide phase, but could be explained by a mechanism in which the growth of the  $\text{Cd}(\text{OH})_2$  film was controlled by transport of mass and charge through the hydroxide layer.
4. Ohse experimented with interrupter measurements, concluding that  $\text{Cd}(\text{OH})_2$  is formed first, and later partially dehydrated to form a CdO layer between the cadmium metal and the hydroxide (83).
5. Falk obtained x-ray diffraction patterns from cadmium electrodes, at various states of charge, immersed in electrolyte (84). He observed no CdO diffraction patterns, indicating that if CdO were present it would

have been in its amorphous condition. He also heated a cadmium electrode to create CdO, then added KOH, while monitoring with x-ray diffraction. Prior to adding KOH, the electrode color was yellowish brown, the acknowledged color of CdO, and CdO diffraction lines were seen. Adding KOH changed the color to the grayish-white color of Cd(OH)<sub>2</sub>, and the CdO diffraction lines weakened within a few seconds. He concludes that if CdO is present as the original anodic species, it is transferred directly into Cd(OH)<sub>2</sub> by the electrolyte. Thus, Falk proposes that cadmium is transformed directly to cadmium hydroxide during anodization.

6. Yoshizawa and Takehara x-rayed cadmium electrodes and, like Falk, found no indications of CdO in the diffraction patterns (85, 86, 87). With electron diffraction, however, they observed diffuse lines from CdO. It has been pointed out, however, that since solutions saturated with CdO were used in this work, there is a reasonable possibility for the CdO to crystallize out prior to the electron diffraction measurements (66). Repeating Falk's experiment, adding electrolyte to an electrode covered with CdO, they obtained similar results with the added finding that it takes a long time for CdO to change to Cd(OH)<sub>2</sub> if the electrolyte is weak in concentration. Their conclusion, not fully substantiated, was that cadmium oxidizes anodically to cadmium hydroxide through an intermediate believed to be cadmium oxide, which is very unstable in KOH solution.
7. Devanathan and Lakshmanan, in experiments on smooth cadmium foil, determined that  $iT^{1/2}$  varied linearly with  $i$  at low discharge current densities, and was constant at high current densities (88).  $T$  is time for passivation at constant discharge current  $i$ . This relationship is consistent with a dissolution-precipitation mechanism in which the passivating step is the formation of an electronically conducting monolayer of oxide. The active intermediate in the passivation reaction is proposed to be CdOH<sup>+</sup>.
8. Armstrong, et al., formed anodic coatings on single-crystal and polycrystalline cadmium and electropolished single-crystal cadmium. They examined the coatings by glancing-incidence electron diffraction and by

electron microscopy. They found no evidence of CdO and concluded that if it is present it must occur as a thin amorphous layer (89).

9. Huber, in tests with a sodium hydroxide electrolyte, found CdO indications in x-ray diffraction patterns, accompanied by a brown color characteristic of CdO (90). He claimed even stronger evidence of CdO in a sodium carbonate electrolyte. If in fact CdO film forms more easily with carbonate present, then an important discovery has been made, for commercial nickel cadmium cells always contain carbonate.
10. Okinaka, using a rotating ring-disc electrode, found evidence indicating that passivation is not the result of complete blocking of the cadmium metal surface with  $\text{Cd}(\text{OH})_2$  crystals, but rather is due to the formation of a thin, continuous film of CdO over metallic cadmium (72). His microscopic observation of the passivated surface showed the coverage with crystalline products to be incomplete. With an oxygen-saturated electrolyte at potentials that are normally passive to the anodic process, he observed reduction of oxygen actually occurring. This could not happen if the surface were completely covered by  $\text{Cd}(\text{OH})_2$ , but it can be explained by a thin film of CdO of high electrical conductivity next to metallic cadmium with  $\text{Cd}(\text{OH})_2$  crystals imbedded in the CdO film. He considered this CdO film responsible for passivation, and it appeared to be insoluble or only very slowly soluble in an alkaline electrolyte.
11. Will obtained a passivating film with a brown color, suggesting CdO, but had no special evidence for specifying either  $\text{Cd}(\text{OH})_2$  or CdO as the cause of passivation (91).
12. Milner and Thomas calculate that an overpotential of at least 36 mV is needed to produce CdO (56). Since such high departures from the reversible potential do not happen often, they claim that it is thermodynamically impossible for CdO to form under conditions that occur in the operation of cells. It should be noted that Ohse has presented a thermodynamic argument concluding that the formation CdO is possible by a chemical process (83). Casey also claims CdO may be thermodynamically possible.\*

\*Private communication, E. J. Casey

13. Armstrong and West view passivation as caused by the formation of a layer of  $\beta\text{-Cd(OH)}_2$  since there is only one discontinuity in the voltage-current curve, and this occurs close to the  $\text{Cd}/\beta\text{-Cd(OH)}_2$  potential where it is thermodynamically "impossible" for  $\text{CdO}$  to be present on the electrode surface (92). They conclude that active dissolution occurs prior to film formation, which occurs through a solid state mechanism.
14. Casey and Gardner withdrew samples of electrolyte from near the cadmium anode, and quickly froze them in liquid nitrogen to stop any hydrolysis, hydration, or protonation which could occur after anodic treatment ceases and during manipulation of the wet sample. After anodic oxidation, they found  $\text{O}_2^-$  predominating at  $25^\circ\text{C}$  and  $\text{O}_3^-$  predominating at  $-40^\circ\text{C}$  (69). Thus, the glassy underlayer appears different at different temperatures. Furthermore, they found an absorption peak representing a second anodic reaction product of cadmium, but the species is not defined. They argue that the appearance of  $\beta\text{-Cd(OH)}_2$  at high temperature and  $\gamma\text{-Cd(OH)}_2$  at lower temperature is coincidental, and that it is the character of the surface states of the elusive and dynamic "CdO" underlayer beneath the  $\text{Cd(OH)}_2$  that determines which of the two oxide species is produced.
15. Jost claims experimental evidence for  $\text{CdO}$  (93). If in a galvanostatic technique the electrode is held at the hydrogen potential, then under certain circumstances, the zeta potential rises to the cadmium oxide potential and then drops.
16. Azim and El-Sobki investigated anodic passivation of cadmium in  $\text{NaOH}$  (94). At sufficiently high overpotential, they obtained a film growth on exposed metal parts which they took to be  $\text{CdO}$ . They consider the Flade potential to be the important threshold for formation of  $\text{CdO}$ .

In summary, it is clear that some type of thin, passivating film is formed during discharge of the cadmium electrode, but it cannot be positively identified as  $\text{CdO}$ . One possible reason why experimental proof of  $\text{CdO}$  has been elusive is the evidence that the passivating film quickly converts to  $\text{Cd(OH)}_2$  during open circuit (79). Experimental techniques that permit in situ examination of composition, structure, and properties of the film are required to settle this point.

### Passivation

Passivation is the phenomenon by which a metal undergoing anodization does not continue to be oxidized even though the potential is adequate and the metal is not depleted. When cadmium is being oxidized at constant current, only a very small over-potential is required until the oxidation layers reach a depth of 100 to 1000 angstroms (78), at which time the potential will rise sharply in the negative direction and the current will go over almost completely into oxygen evolution. Then the metal is said to have then become passivated.

If the oxidation is carried out at constant potential, the electrode behavior depends on whether or not the potential exceeds the potential of passivation. At potentials lower than the potential of passivation, current density is low, but the discharge capacity is high (93). At potentials greater than the potential of passivation, current density is high and capacity is low, and the current decay with time is close to the theoretical  $I = f(t^{\frac{1}{2}})$ , which is indicative (but not proof) of film growth according to a parabolic growth law (93, 82). Current-voltage sweeps always produce a high anodic peak (79, 93, 92, 82, 72,

94), showing an active region and a passive region due to film formation. Evidence relating to the possible existence of a CdO film was summarized in the previous part of this section.

The fact that cadmium passivates on anodization (discharge) is important because it means that the electrode capacity limit is reached before all the active material is fully discharged. In a normally operating nickel cadmium cell, the cadmium electrode is not fully discharged, and so the passivation point would indicate the amount of cell capacity that is not being used and hence available as reserve. In some battery applications passivation occurs regularly, for example in a cell designed to be negative limited (95), in a cell that has unintentionally become negative limited, in a cell operating at low temperature, in high discharge rate applications, and during cell reversal. If passivation could be delayed, then more of the active material could be utilized, and the energy density of the cell would be higher.

When cadmium is anodized (discharged) at constant current, the potential rise indicative of passivation precedes the evolution of oxygen. The overpotential gradually increases to about 0.9 volts, followed by oxygen evolution which typically is in the range of 80 to 100 percent of theoretical gassing efficiency (79).

The time to passivate is reported variously as (a) the time elapsed before an abrupt voltage change (96), (b) the time for a potential change of 0.4 volts (97), or (c) the time to reach a relatively constant oxygen evolution potential (79). The product of passivation time and discharge current is proportional to the amount of cadmium oxidized, and hence the discharge capacity of the plate. The discharge efficiency of the plate can be calculated from a comparison of the mass of the oxidized cadmium with the theoretical maximum.

The discharge capacity before passivation occurs is greatest under these conditions: (1) low current density, (2) optimum KOH concentration (or near-zero KOH concentration), (3) high temperature, (4) electrolyte contains  $K_2CO_3$ , (5) electrode contains indium, especially if at low temperature, and (6) optimum plate pore size and porosity.

The single most important contributor to a high discharge capacity prior to passivation is low discharge current density (Fig. 3-1). Low discharge rates produce large crystals, but the reduction in available sites for anode products is more than offset by the fewer sites needed at low rates. However, if the charge rate is high, then the discharge rate is less important (98, 99).

With sintered electrodes, the greatest capacity before passivation is obtained with 7 N KOH as shown in Fig. 3-2 (98). With planar non-porous electrodes, very high KOH concentration gave the highest capacity (Fig. 3-3) due to improved crystal structure, resulting in uneven development of the films, with much of the surface covered by layered growth (97). Thicker parts grew preferentially but the point of oxygen evolution was not reached until the thinnest parts thickened. This difference in behavior between sintered and planar electrodes is unexplained, but could be due to the high discharge rate (2.5 C) on the sintered electrode.

The reason why carbonate ions delay passivation is not understood, but may be related to the fact that the product of discharge contains cadmium carbonate in addition to cadmium hydroxide. No explanation has been reported for the delay in passivation at high temperature (96, 97). Gravity appears to have no significant effect on the passivation process, based on tests on planar electrodes in which electrode position was changed (97).

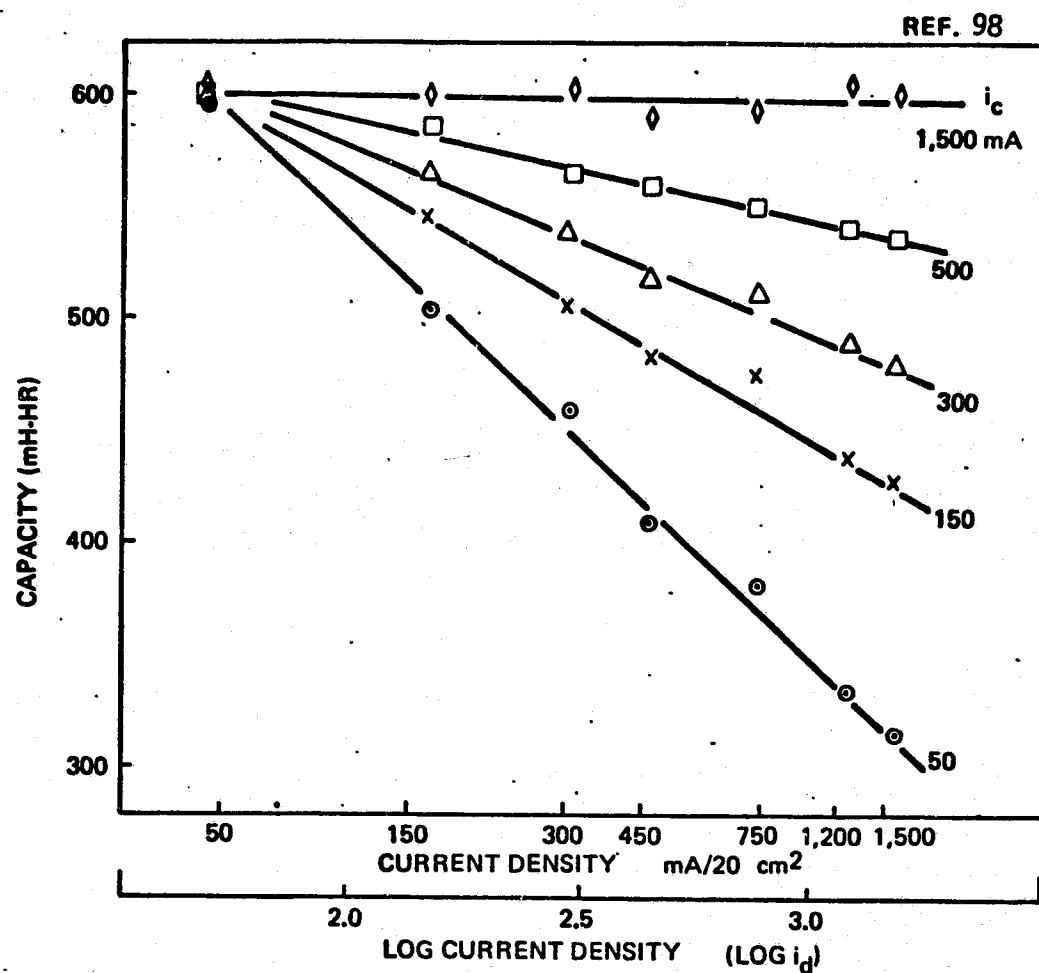
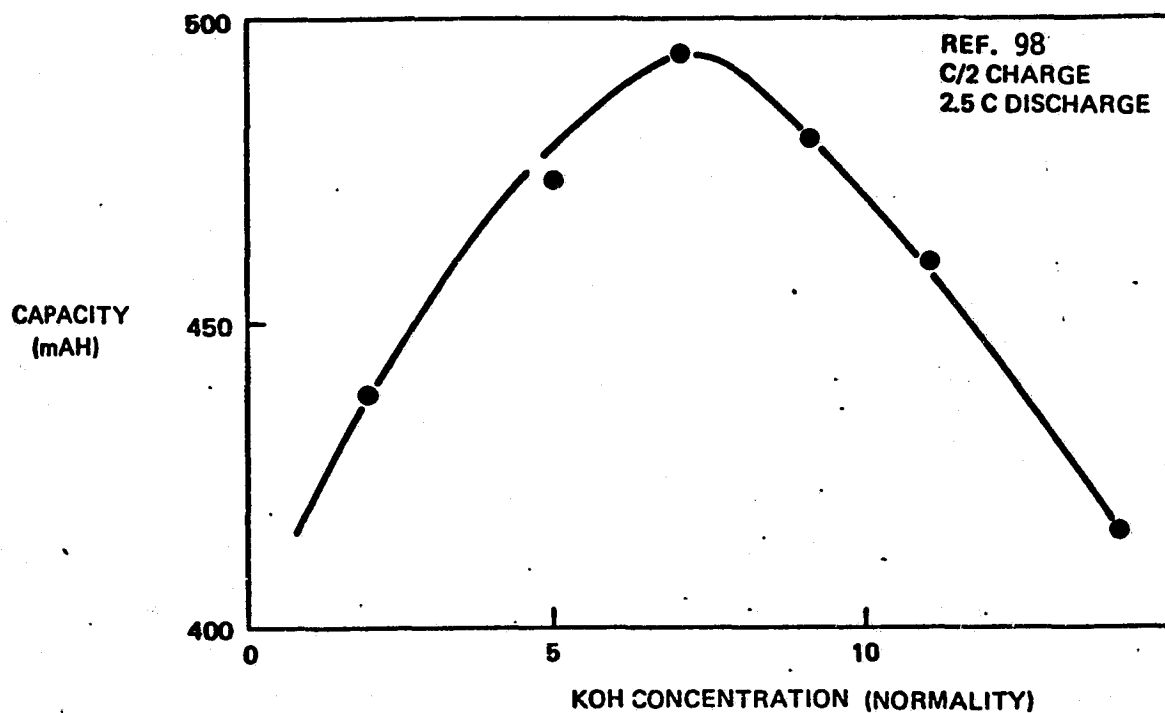
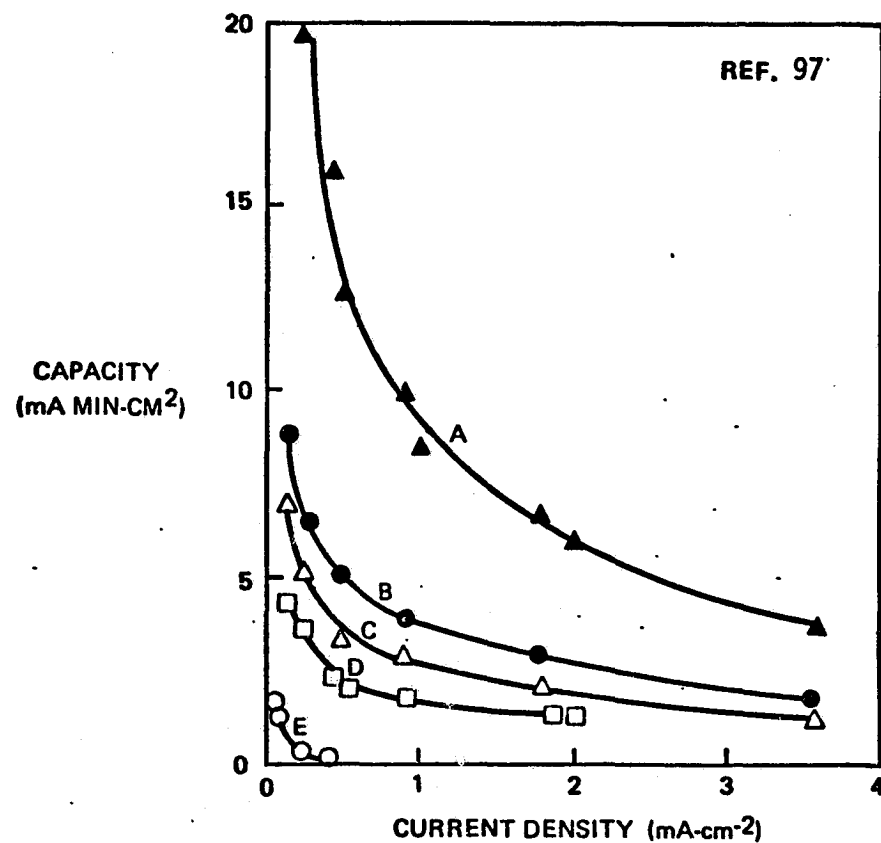


Figure 3-1. Variation of Capacity With Discharge Current for Various Charging Currents





*Figure 3-2. Effect of Potassium Hydroxide Concentration on High Rate Capacity*



25°C: A-13.6M KOH, B-9.0M KOH, C-5.0M KOH, D-3.0M KOH, E-1.0M KOH

**Figure 3-3. Effect of Electrolyte Concentration on Capacity of Planar Cadmium Electrodes**

The addition of indium has improved the efficiency of the negative electrode, even permitting the use of relatively thick electrodes (1). Sweeping-potential studies show that this improvement results from a 20 mV delay in the passivation point (82). The precise mechanism of indium action is not known, but it is believed that some indium incorporates into the cadmium hydroxide crystal lattice, creating more imperfections. The effects of indium are discussed in detail in the section on impurities.

If the discharge of a cadmium electrode is interrupted by open-circuiting before passivation, and later the discharge is continued, the net result is the same as if there had been no open-circuit period (97). However, if a passivated electrode is open-circuited, it becomes depassivated and can sustain a small additional discharge. Apparently some of the passivating film is removed or changed to non-passivating film during stand (79). Analysis suggests that the passivating CdO layer was converted during open circuit to  $\text{Cd}(\text{OH})_2$ , explaining why CdO has been detected only under carefully chosen conditions.

The capacity of a porous electrode depends upon the pore volume that is accessible to the electrolyte (100). Tests of porous cadmium electrodes made by compressing cadmium dendrites (96) showed that with below-optimum porosities, passivation occurs when the void fraction reaches a critical minimum. This minimum void fraction increases with current density, being 0.32 for  $8 \text{ mA/cm}^2$  and 0.44 for  $40 \text{ mA/cm}^2$ . The apparent cause is poor mass transfer in pores (100, 101, 102, 102A, 102B, 103). Anodes with above-optimum porosities passivate when the volume fraction of metallic cadmium decreases to a critical value, this being apparently caused by low electronic conductivity of disruptions of structure, and by decreased surface area of cadmium particles.

Kang measured passivation time for planar cadmium electrodes at temperatures down to  $-60^\circ\text{C}$  (104). He correlated his data at low current densities by a linear dependence of  $iT^{1/2}$  with  $i$ , where  $T$  is the passivation time at constant current density  $i$ . His correlation suggests that the low temperature limit is at the vitreous point,  $165^\circ\text{K}$ .

Insight into the passivation process internal to porous cadmium electrodes can be gained from experiments by Bro and Kang (105). Electrodes were made by sintering spherical cadmium particles, and discharge profiles were determined by chemical analyses of thin sections sliced from the electrodes. The results showed

that at high current densities the inner parts of the electrodes ceased to participate in the discharge. The discharge initially affected surfaces of the electrodes, then subsequently penetrated into the interior (93). Accumulation of the discharge products inside the porous structure choked the pores, obstructing mass transfer, especially at low current densities. Thus, the abrupt increase in polarization at the end of discharge might be attributable to either a film-type electrochemical passivation, to mass transfer limitations, or to a combination of both.

A passivation and electrode-inefficiency explanation that does not require the concept of a CdO film, proposes instead a film of  $\text{Cd}(\text{OH})_2$  (74). Cadmium metal is first postulated to dissolve as  $\text{Cd}(\text{OH})_4^{-2}$  which then precipitates as solid  $\text{Cd}(\text{OH})_2$ . As the discharge proceeds, the area of active cadmium is reduced both by its dissolution and by blocking of the electrode surface by  $\text{Cd}(\text{OH})_2$ . The overpotential increases until it is high enough for  $\text{Cd}(\text{OH})_2$  to grow directly onto the cadmium. This film grows, and oxygen evolution starts when further film growth cannot be sustained.

Another possible explanation of passivation is that the cadmium hydroxide formed near the end of discharge has a high resistivity structure which hinders further discharge. This structure is hexagonal, but has no bridged  $\text{OH}^-$  groups, whereas the normal active cadmium-hydroxide form has bridged  $\text{OH}^-$  groups (34). The high resistive form could occur locally where the  $\text{OH}^-$  ion concentration is low as a result of reduced porosity during discharge.

In summary, a rigorous explanation of passivation is not yet possible. Much of the evidence on passivation is indirect and can have more than one interpretation. A better understanding of passivation is important, for it is now a fundamental limiter of the efficiency of the cadmium electrode. Many of the experiments reported in the literature were based on cadmium electrodes that had been fully charged and fully discharged, whereas this does not happen in normal sealed cells. Future investigations might will focus on the realistic operating regime of the cadmium electrode.

#### Charge Behavior

Because of the importance of the passivation during discharge, most of the research on the cadmium electrode has related to the anodic processes. The

cathodic charging process, by contrast, has received less attention even though the user usually has more control of charging conditions than he has of discharging.

One basic question is: Does the cathodic reduction occur by a solid state mechanism or is a solution phase involved? Okinaka showed that both mechanisms occur, the solid state mechanism predominating at the start of the charge when there is little cadmium metal, and the solution-reduction mechanism predominating at the end of charge when there is much cadmium (72). This was confirmed by Will (106). Experiments in reducing cadmium oxide showed that electrolyte concentration plays a role, with solid phase reactions predominating at low concentrations, and combined solid-phase/solution-phase reactions occurring at high concentrations as solubility increases (72).

The physical condition of the cadmium electrode, especially crystal size, is particularly important to electrode behavior during charge. This is discussed in detail in the section on cycling. At the start of charge, with little exposed metal area for cadmium deposition, current density is high and overpotential can be high. During mid-charge, overpotential is low because there is plenty of cadmium metal surface area and cadmium hydroxide surface area available for the reaction. At the end of charge, the overpotential again increases because of less available  $\text{Cd(OH)}_2$ . A high charge rate during most of the charging period, which can be accompanied by high overpotential, is advantageous in that it generates many nuclei, and hence many small cadmium crystals. At extremely high rates there is a risk of premature hydrogen evolution.

High charge and discharge rates and low temperature are effective in promoting small crystals (98, 58, 107), but cycling generally makes crystals bigger (98, 85, 108). Some cadmium hydroxide crystals crack at the surface (108) breaking down into smaller ones during charge. Charge acceptance is highest if the cadmium hydroxide crystals are small at the start of charge, and if the preceding discharge was at a high rate and low temperature (107, 58).

Charging at low temperature can promote hydrogen evolution, which is discussed in another section. Low-temperature discharge produces gamma cadmium hydroxide in addition to the usual beta cadmium hydroxide (109, 110). The gamma form, having needle-like crystals, is much more easily charged than is the beta form (110). "Inactive" and "active" forms of cadmium hydroxide have been reported at low

temperature by Rubin (111). These probably were the beta and gamma forms, respectively. Different potential plateaus reported for these two forms (111) have not been observed by others (110). There is a possibility, however, that Rubin's "inactive" form is related to the high resistivity form noted by Appelt (34) and discussed previously.

The fact that the gamma form is more easily charged is very significant (110). Discovering a way to generate gamma cadmium hydroxide during room-temperature discharge would substantially improve the performance of nickel-cadmium cells.

A low temperature effect not to be neglected is the high efficiency of the nickel positive plate, which reduces the effective negative-positive ratio. For example, the capacity of the cadmium electrode at  $-7^{\circ}\text{C}$  is about 77 percent of its capacity at  $21^{\circ}\text{C}$  (98). The nickel positive electrode, in contrast, has about 30 percent more capacity at  $-7^{\circ}\text{C}$ , making the negative-positive capacity ratio less for the lower temperature. Cells designed for low temperature require a greater amount of negative active material, and when properly designed have operated successfully at  $-40^{\circ}\text{C}$  and colder (112).

One important factor in applying to sealed cells the results from charge and discharge studies on experimental electrodes is that those electrodes are usually fully charged and discharged. The negative electrodes of sealed cells never get fully charged. Fully charging a cadmium electrode is known to be harmful, causing agglomeration of metallic cadmium (108).<sup>\*</sup> This factor appears not to have been fully considered not only in electrode studies but also in choosing the pre-charge level of sealed cells.

#### Electrolyte Effects

Electrolyte reactions and mass transfer within a sealed nickel cadmium cell significantly affect cell operation. Although these effects are understood qualitatively, little has been done to incorporate participation of the electrolyte into the reaction equations, to calculate electrolyte changes, or measure local concentration or the effects of major variables. Changes in average concentration of electrolyte have been calculated (109), but little consideration was given to the large local variations in concentration. Concentration effects at the cadmium electrode are important because the electrode operates primarily by dissolution-precipitation, and solubility of cadmium species is electrolyte concentration

<sup>\*</sup>Also, private communication, D. Bro 44

dependent. It may in fact be possible to use electrolyte concentration changes in optimizing storage of nickel cadmium cells.

During charge, water is generated at the nickel electrode and at the cadmium electrode are generated hydroxyl ions which are consumed at the nickel electrode. The overall effect is to lower average electrolyte concentration in the cell during discharge (Fig. 3-4); however, initially the concentration must increase at the cadmium electrode. Because of the hydroxyl ion transfer from negative to positive electrodes during charge, there must be a concentration gradient which reaches a steady state condition during overcharge. This overall concentration gradient adds to the gradient that occurs within the pores of the electrodes. During discharge the process is reversed. From these qualitative considerations, one would expect that the highest local concentration at the cadmium electrode would occur early during charge following a period of open circuit, and conversely that the lowest local concentration at the cadmium electrode would occur early during charge following a period of open circuit.

Another important change in electrolyte concentration results from setting the precharge in cells. When precharge is set by venting oxygen prior to sealing the cell, the net effect is to lower electrolyte concentration by about 0.8 percent (109). No calculations or test data are reported on the electrolyte changes that occur when precharge is set by overcharging the negative electrode with the cell case as a counter electrode.

#### Thermal Effects

The overall charge process in a nickel cadmium cell is generally endothermic, except during overcharge or when the charging potential exceeds approximately 1.44 volts (113). During overcharge, most of the heat is generated at the negative by the oxygen recombination. The endothermic reaction occurs at the nickel electrode, whereas the cadmium-electrode reaction is exothermic even during charge. This is apparent from the negative entropy of the reaction of equation (3-1), the entropy change having a value of  $-15.5 \text{ cal/}^{\circ}\text{K}$ , and the term  $T\Delta S$  having a value of  $-86 \text{ cal/A-Hr}$  (113).

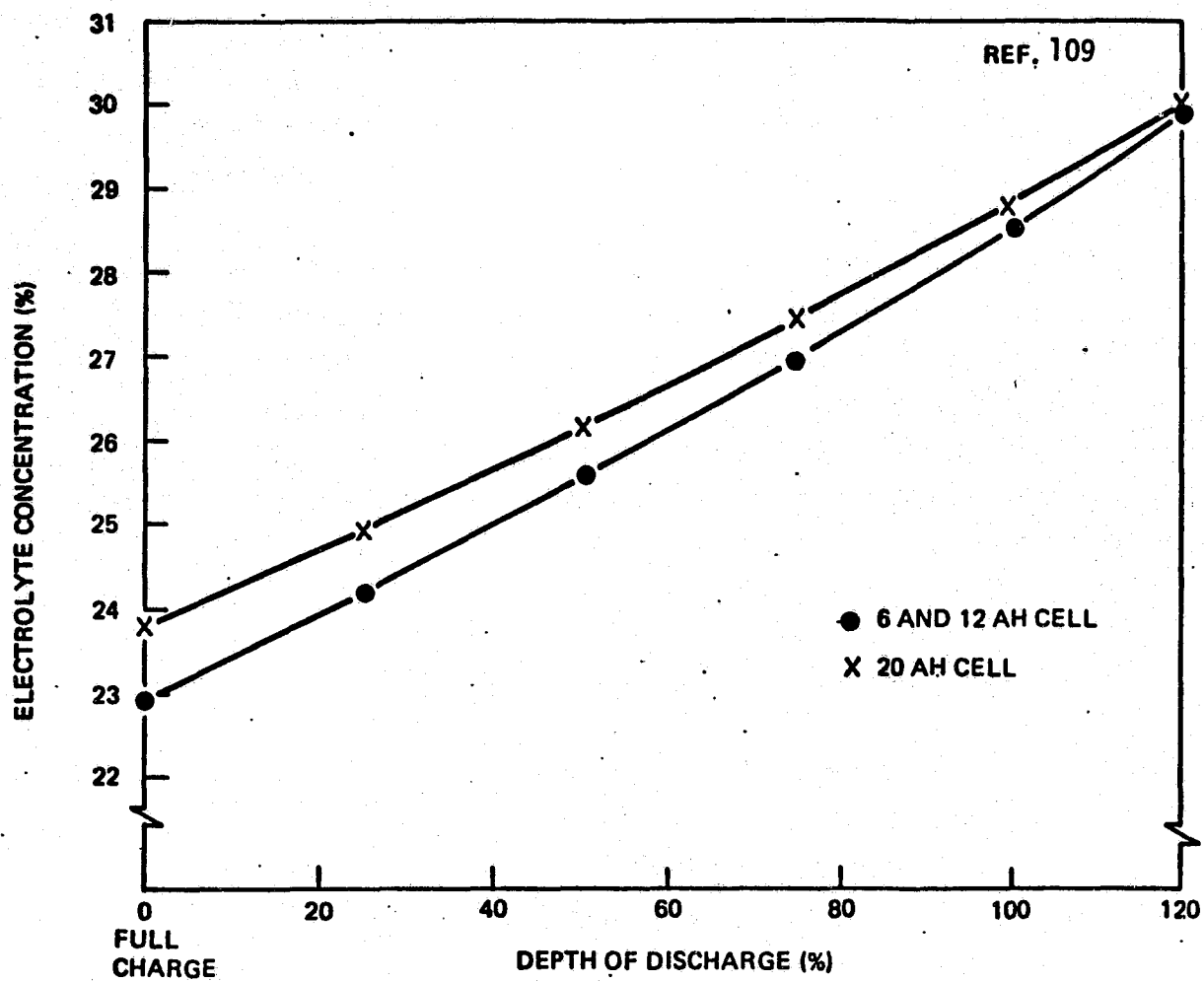


Figure 3-4. Depth of Discharge versus Electrolyte Concentration



No information is available on effects that might be caused by local heating of the cadmium electrode during charge, and local cooling during discharge. However, it is apparent that this would create in the cadmium electrode small temperature gradients which could contribute to driving cadmium migration toward the electrode surface.

#### 4.0 PROPERTIES OF CADMIUM MATERIALS

Cadmium is the most important component of the negative electrode. In the NiCd cell it occurs in several allotropic forms. Cadmium oxide and cadmium hydroxide in their various crystal and allotropic forms are also present. The properties of cadmium and its compounds are described in the paragraphs that follow.

##### Metallic Cadmium

Metallic cadmium is produced during charging of the cadmium negative electrode. The literature defining the properties of cadmium is voluminous, extending back into the 19th century. For detailed information, the reader is directed especially to references 114, 9, 74, 115, and the references cited therein.

In color, metallic cadmium is silver-white with a blue tinge. Finely divided cadmium is grey-black. The metal is isomorphous, in that its crystals have axes of the same relative lengths and included at the same angles. The crystals are bipyramidal and belong to the hexagonal system, with an axial ratio  $c/a = 1.89$ , compared with the ideal close-packed ratio of 1.63 (Ref. 66). The lattice parameters are  $a = 297.93$  and  $c = 561.81$  pm\* (Ref. 66). Crystals when formed as dendrites are six-rayed stars, with branches at  $60^\circ$  angles, preserving hexagonal symmetry. The crystalline structure is not entirely lost during mechanical treatment, such as hammering, rolling, and drawing. Cold-worked cadmium annealed at a temperature of about  $200^\circ\text{C}$  forms into large crystals, but recrystallization can also occur even at room temperature. Specific gravity of metallic cadmium is 8.65. When annealed, the metal contracts slightly, and expands when cold worked. Like tin, cadmium produces a peculiar crackling sound when bent.

There are at least three allotropic forms of cadmium. The metastable gamma form occurs during electrolytic deposition, changing in time into the alpha form, which is stable from  $20^\circ\text{C}$  to  $65^\circ\text{C}$ . Above  $65^\circ\text{C}$ , the beta form is stable. The gamma form is the higher energy state, having greater heat of dissolution and having an emf about 3 mV greater than the alpha form.

Some of the physical constants of cadmium are given in Table 4-1. The Faradaic equivalent of cadmium is 0.477 ampere-hours per gram (Ref. 57). Cadmium is very flexible and can be cut with a knife, drawn into wires, or beat into plates.

\*pm = picometers =  $10^{-12}$  meters.

At 80°C it becomes very brittle and is easily powdered. Both electrical and thermal conductivity increase as temperature is reduced. The 321°C melting point of cadmium in vacuum results in a high sublimation rate.

Table 4-1 Physical Properties of Cadmium (54)

Brunell Hardness	29.0
Modulus of Elasticity	$467 \times 10^6$ grams/cm <sup>2</sup>
Bulk Modulus	$4.12 \times 10^{11}$ dynes/cm <sup>2</sup>
Poisson's Ratio	0.30
Plasticity	31.0 kilograms/mm <sup>2</sup>
Coefficient of Linear Expansion	$2.98 \times 10^{-5}$ (0°C to 100°C)
Coefficient of Cubic Expansion	$9.4 \times 10^{-5}$ (0°C to 40°C)
Thermal Conductivity	0.22 cal/cm <sup>2</sup> -sec-°C
Specific Heat	0.0546 (increases with temperature)
Melting Point	321°C
Specific Conductivity	$13.1 \times 10^4$ (ohms) <sup>-1</sup>
Magnetic Susceptibility	$-0.17 \times 10^{-6}$ (18°C)

The electrical conductivity of cadmium is about 23 percent of that of silver. Cadmium exhibits a strong Faraday effect in that the plane of polarization rotates in a magnetic field.

Cadmium films have been found to occlude some hydrogen. Cadmium remains bright in dry oxygen or dry air at room temperature. The bright luster of cadmium soon dulls when exposed to air containing moisture and carbon dioxide. The grey film that forms when carbon dioxide, moisture, and oxygen are present is very tenacious, and slows down oxidation of the underlying metal. Cadmium also burns when heated in air and is readily attacked by ozone. Colloidal solutions of minute cadmium metal particles can occur but are unstable and coagulate when in electrolyte (9).

There are eight isotopes of cadmium, many of them common, affecting its atomic weight. Cadmium is a good absorber of low energy neutrons, and thus is used to control nuclear reactors. Metallic cadmium is almost completely insoluble in basic solutions (70), and no appreciable concentration of Cd<sup>2+</sup> can exist. Soluble species of cadmium compounds are discussed elsewhere in this report.

The purity of commercial cadmium can range from 99.5 percent to greater than 99.9 percent. Major impurities are zinc, lead, copper, iron, arsenic, and sulfur.

#### Cadmium Oxide (CdO)

The material properties of cadmium oxide are important because of the evidence, though still equivocal, indicating that CdO is a substantial intermediate in the passivation of the cadmium negative electrode. Cadmium oxide is also used in some processes for manufacturing cadmium electrodes.

Cadmium oxide has a nominal molecular weight of 128.4, a density of  $8.15 \text{ gm/cm}^3$ , a specific heat of  $0.081 \text{ cal/gm } ^\circ\text{C}$ , and a Faradaic equivalent of 0.417 ampere hours per gram (57). The Hall coefficient has been studied (116). It has a face-centered cubic lattice, as does sodium chloride. The oxide is an n-type semiconductor with nearly metallic conductivity (116); bulk CdO has a conductivity ranging from 100 to  $500 \text{ ohm}^{-1}\text{cm}^{-1}$  (117).

Cadmium oxide has an excess of cadmium relative to stoichiometric; the greater the departure from the stoichiometric composition, the greater the electrical conductivity (118). It is not known, however, whether the excess of cadmium is due to interstitial cadmium ions or oxygen vacancies. As the amount of excess cadmium increases, the lattice parameter also increases (119) which increases the random diffusion coefficient. Small additions of indium can incorporate into the crystal lattice and increase the lattice parameter (120). This change in lattice parameter may relate to the performance improvement observed in cadmium electrodes with indium (1).

Silver (120) and lithium (121, 102) can also be incorporated into the crystal lattice of cadmium oxide. Silver contracts the lattice parameter, and lithium increases oxygen self-diffusion. Both silver and lithium are found at times in nickel cadmium cells.

#### Cadmium Hydroxide

Cadmium hydroxide is produced during cell discharge and it also exists at all times in the cadmium negative electrode. Its nominal molecular weight is 92.95 (note that cadmium has eight common isotopes which affect molecular weight). This hydroxide has a density of  $4.79 \text{ gm/cm}^3$ , and a Faradaic equivalent of 0.366 ampere hours per gram (57). Electrochemically produced cadmium hydroxide is pale yellow, whereas solution precipitated cadmium hydroxide is white.

X-rays will bleach the pale yellow hydroxide to white, indicating the presence of defects in the  $\text{Cd}(\text{OH})_2$  lattice (122). The hydroxide is a p-type semiconductor. There appears to be no data on its electrical conductivity, but surface resistivity has been reported to be 20 megohms (123).

Beta and gamma cadmium hydroxide exist in electrodes. The beta type is the more stable, especially at room temperature, while the gamma type is observed most readily at lower temperatures (107, 69, 124). The beta phase has a density of  $4.78 \text{ gm/cm}^3$ , whereas the gamma phase has a density of  $4.81 \text{ gm/cm}^3$ .

Beta cadmium hydroxide is a close-packed hexagonal layered crystal of brucite structure with one molecule per unit cell. The lattice parameters are  $a = 349.6$  and  $c = 470.2 \text{ pm}$  (66). When the beta phase is formed on a single cadmium crystal, the crystal layer of the hydroxide is oriented parallel to the cadmium (125). In the development of the first few crystal layers of hydroxide, the crystals grow slowly forming the lattice at the periphery of two-dimensional growing centers (125). The mono-molecular layers deposit successively, with the  $c$  axes of the metal and hydroxide being parallel (89). If the over-voltage exceeds 20 mV, the beta cadmium hydroxide formed on a single cadmium crystal is two-degree oriented; otherwise, it is one-degree oriented (89). On polycrystalline cadmium the cadmium hydroxide forms randomly oriented crystals.

Gamma cadmium hydroxide is monoclinic, having four molecules per unit cell (126). The structure has roughly octahedral coordination, with the octahedra in pairs, each pair sharing the mirror plane. All Octahedra share edges with both neighbors in the  $c$  direction and are arranged in double strings along the  $c$  axis. The lattice parameters (66) indexed on the basis of an I-centered unit cell are:

$$\begin{aligned} a &= 567 \text{ pm} \\ b &= 1025 \text{ pm} \\ c &= 341 \text{ pm} \\ \alpha &= \gamma = 90^\circ \\ \beta &= 91.4^\circ \end{aligned}$$

Although beta cadmium hydroxide is generally considered a physically unique material, it has been reported that there are two kinds of cadmium hydroxide with the same hexagonal crystal structure (34). The first type, precipitated from very concentrated and hot solutions of  $\text{CdI}_2$  and  $\text{KOH}$ , has a sheet secondary structure, no bridged OH groups, is passive to electrochemical reduction, and has a very high resistivity. The second type, precipitated for example from  $\text{Cd}(\text{NO}_3)_2$  and  $\text{NaOH}$  solutions at ambient temperature, does not have a sheet structure, but has bridged OH groups and is active to electrochemical reduction. It has been postulated (99) that the high resistivity form can be produced within electrodes when the OH concentration is low, as might occur in choked pores.

## 5.0 HYDROGEN EVOLUTION

### General Principles

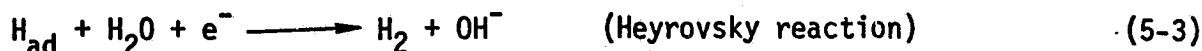
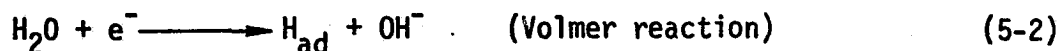
During charging of vented nickel cadmium cells, oxygen evolves at the positive electrode and hydrogen evolves at the negative electrode. In sealed nickel cadmium cells, however, hydrogen evolution is intolerable, and is prevented by design features and operation restrictions.

Hydrogen, if generated in a sealed cell, is consumed only at extremely slow rates, and unrestrained hydrogen production will quickly deform the cell case. Lunn and Parker (127) have found that hydrogen reacts slowly with charged nickel positive active material (Fig. 5-1) and they have proposed a set of reactions describing the gas recombination.

The overall reaction for hydrogen generation in an alkaline solution is



The reaction rate will be determined by one of these steps (7):



Theoretically, the cadmium electrode should generate some hydrogen when the cell is open circuited, and even more during charge as the electrode potential becomes more negative because of the high overvoltage\* associated with charge current. The theoretically possible equilibrium hydrogen pressures are given in Table 5-1, reproduced from reference 56. In practice, cadmium has such a high hydrogen overvoltage that no significant amount of hydrogen is produced at the theoretical voltages. The data in Table 5-2 show the effect of temperature and electrolyte concentration on the theoretical gassing potential at one atmosphere (7).

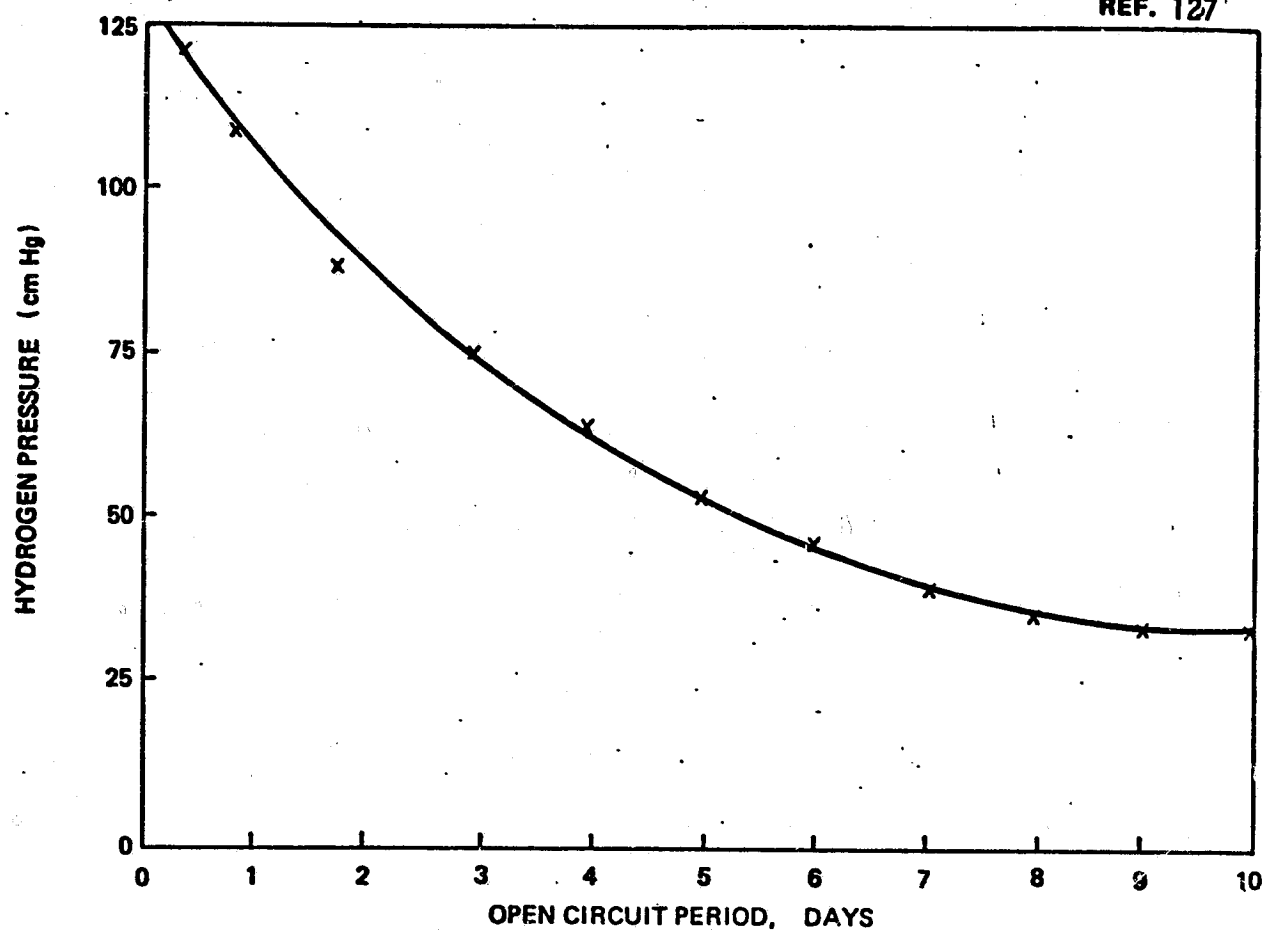
These data show that the gassing potential is only slightly sensitive to the temperatures and KOH concentrations normally experienced in nickel cadmium batteries.

Hydrogen overvoltages measured on smooth cadmium metal (7), shown in Fig. 5-2, indicate that the overvoltage must exceed 0.5 volt before much gassing reaction takes place. This high overvoltage results from the

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\*Hydrogen overvoltage is defined as the difference between the theoretical potential at which hydrogen evolution should occur and the observed potential at which it does occur, at one atmosphere pressure.

REF. 127



*Figure 5-1. Decay of Hydrogen Pressure in Cell With Positive Active Material Only.*



TABLE 5-1: THEORETICAL EQUILIBRIUM HYDROGEN PRESSURE ON CADMIUM ELECTRODE

Based on Ref. 56

Cd/Cd(OH) <sub>2</sub> Overvoltage (negative)	Voltage vs. Hg/HgO (30% KOH, 25°C)	Theoretical Equilibrium Pressure
0	-0.899 V	0.073 atm
34 mV	-0.933 V	1.00 atm
63 mV	-0.962 V	10.00 atm

Ref. 7

TABLE 5-2: REVERSIBLE POTENTIAL FOR HYDROGEN EVOLUTION PROCESS

KOH	TEMP. °C	E <sub>rev</sub> , CALCULATED
6N	2	-0.937
6N	25	-0.932
6N	50	-0.924
9N	25	-0.938

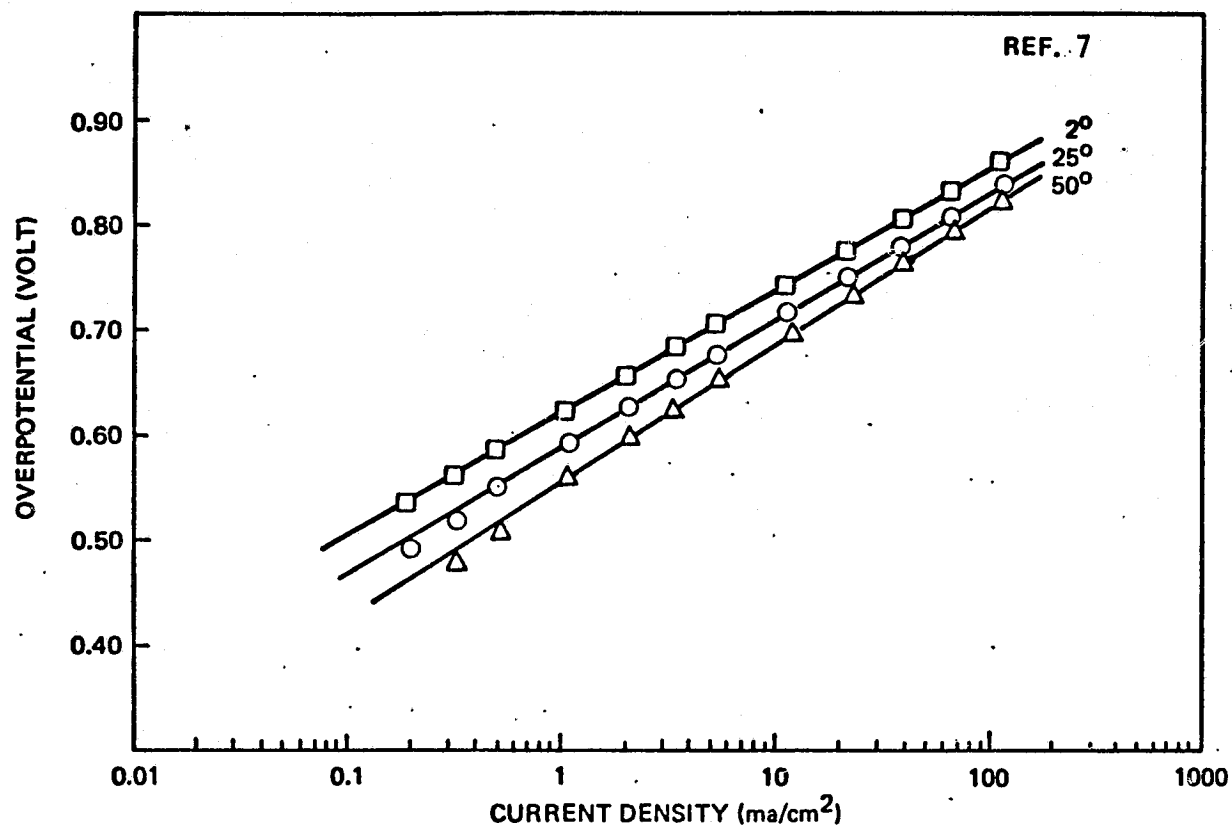


Figure 5-2. Hydrogen Overpotential on Smooth Cd in 6N KOH

low heat of adsorption of atomic hydrogen on cadmium (128). Mercury has an even higher hydrogen overvoltage, but most other metals will promote gassing more readily. Calcium, magnesium and silicon ions reduce the hydrogen overvoltage on cadmium, and are therefore undesirable impurities (129, 130).

Nickel has a lower overvoltage for hydrogen evolution than does cadmium. Hydrogen evolution on smooth surfaces of cadmium, silver and nickel are compared to Fig. 5-3 (50). Any exposed nickel substrate or plaque is a site for hydrogen evolution, were it not partially passivated. In Boeing tests freshly generated nickel on a cadmium electrode gassed more than did nickel that has been exposed to a charge-discharge cycling environment. Some of the occasional unexplained cell ruptures may have been caused by hydrogen released on exposed nickel substrate.

Silver's high overvoltage for hydrogen generation has been exploited in a low gassing cadmium electrode in which silver replaced nickel used in the plaque (50). Cadmium electrodes that use cadmium substrates instead of nickel have also been used to reduce hydrogen gassing (39, 130A).

Oxygen recombination at the cadmium electrode has an important effect on hydrogen generation. This recombination process depresses or makes less negative the voltage at the cadmium electrode, reducing the likelihood of hydrogen generation. Further charging of the cadmium electrode stops at this time. If the charge rate is not reduced quickly enough at the end of charge, the negative potential can rise to the point where hydrogen evolves before the voltage is suppressed by the oxygen recombination reaction (Fig. 5-4). Hydrogen can also evolve if oxygen recombination is poor, caused for example by too much electrolyte or pores being so small they flood easily. Thus, a cell which is well designed with respect to oxygen recombination will be less likely to generate hydrogen. Good oxygen recombination is obtained by limiting the quantity of electrolyte, and by not loading the pores so heavily that they will easily flood with electrolyte, reducing accessibility of oxygen (131, 132, 133).

Design features that prevent hydrogen generation during charge are:

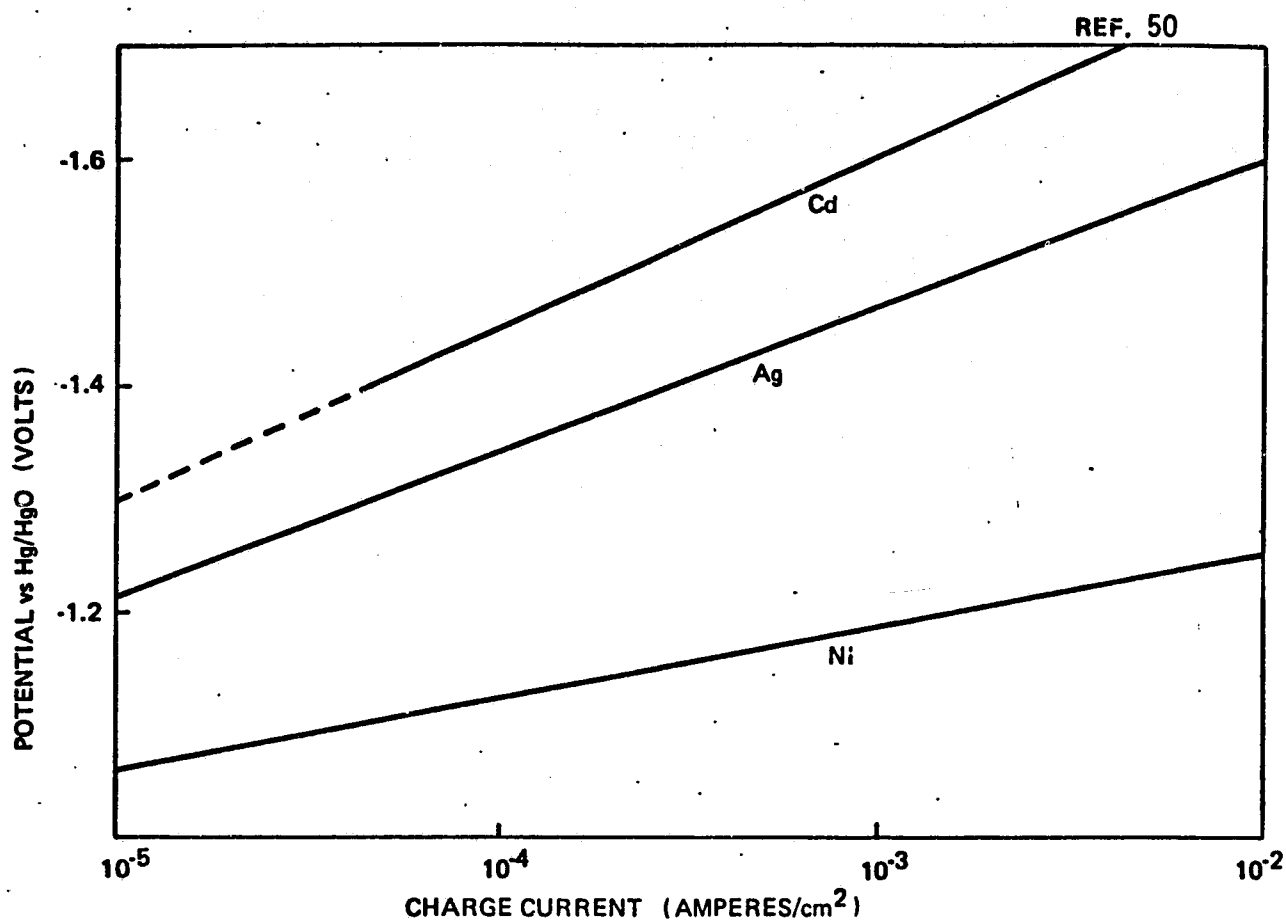


Figure 5-3. Evolution of Hydrogen on Cadmium, Silver, and Nickel, 25% KOH, Room Temperature

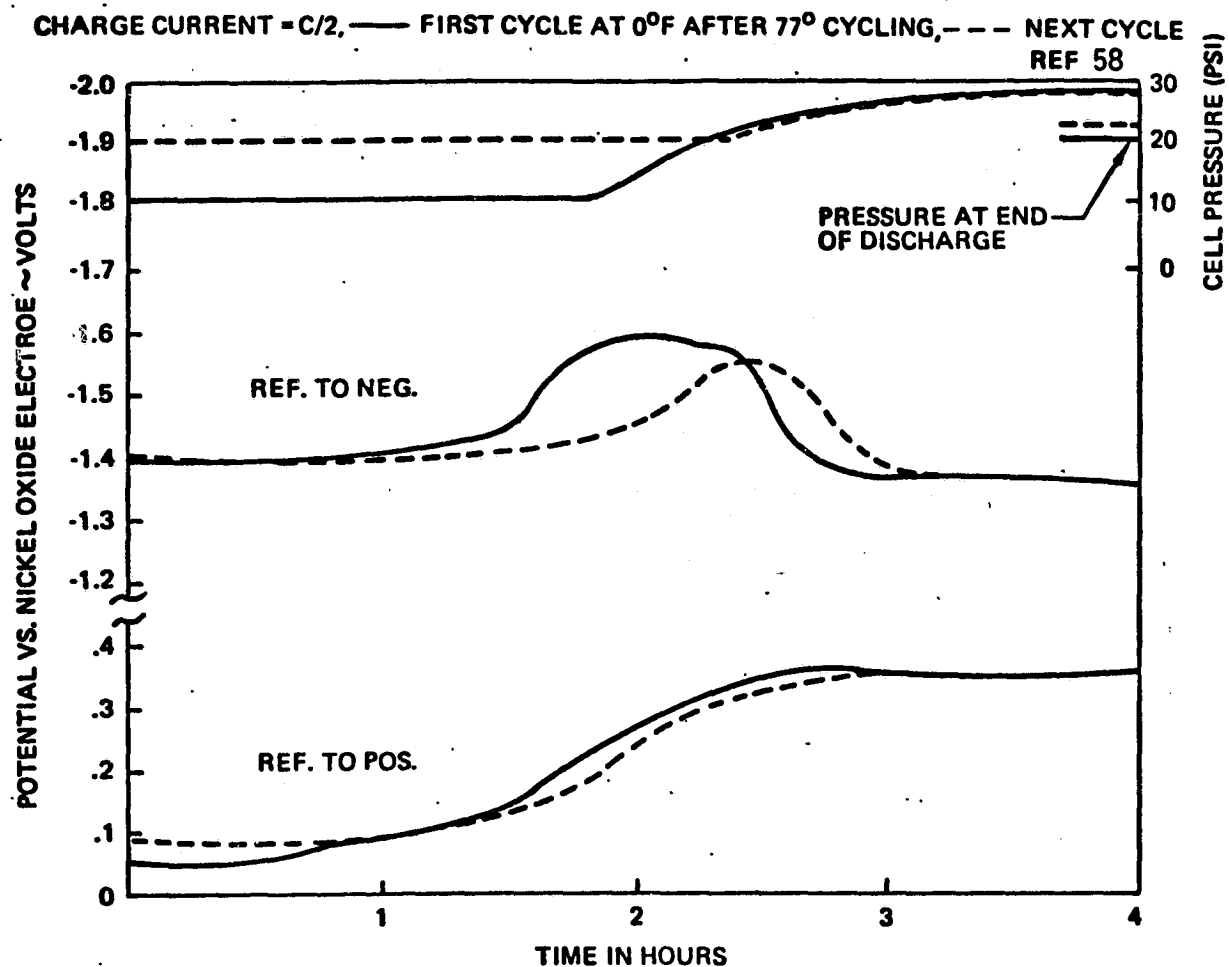


Figure 5-4. Electrode Voltage of Nickel Cadmium Cells During Charge at 0°F

- (1) Making the capacity of the negative plate much greater than that of the positive plate, so that oxygen will evolve at the positive electrode before the negative plate is fully reduced and can evolve hydrogen.
- (2) Enhancing the kinetics of the oxygen-gas-consuming reaction, mainly by limiting electrolyte to a semi-starved condition.
- (3) Adjusting the relative states of charge of the positive and negative electrodes so that the positive electrodes always become fully charged first.
- (4) Adding auxilliary hydrogen recombination electrodes to the cell if necessary (Ref. 134).

There are five different operating conditions during which hydrogen can evolve in nickel cadmium cells:

- (1) From the nickel positive plate during cell reversal.
- (2) From the cadmium negative plate at the beginning of charge.
- (3) From the nickel substrate of the cadmium negative plate at or near the end of charge.
- (4) From the cadmium plate at or near the end of charge.
- (5) From the electrolyte during irradiation.

These hydrogen sources are discussed below.

#### Hydrogen from Nickel Positive Plate

Hydrogen is generated from the nickel positive plate during reversal of a positive limited cell, with onset occurring within a cell potential between zero and -0.25 volts, depending on current. In a negative limited cell undergoing reversal, oxygen will first evolve from the negative plate. If the oxygen can recombine fast enough at the positive electrode, hydrogen gas will not be released. The ability of the discharged positive plate to recombine oxygen has received very little study, but there are indications that it has this capability under some conditions (135, 136, 137, 138). Antipolar mass, such as cadmium hydroxide added integrally to the positive plate, will promote recombination if there is enough mass to last until the negative plate is depleted (139, 57). Part of the antipolar mass is changed to metallic cadmium, whereupon the oxygen evolved from the negative

plate reacts with the antipolar mass to maintain a steady-state condition.

#### Hydrogen From the Negative Plate at Start of Charge

Nickel-cadmium cells are generally thought to be tolerant to high charge rates, at least until about half charged. However, under some conditions hydrogen can evolve at the very beginning of charge, long before the positive electrode becomes fully charged (140, 141, 58). This poor charge acceptance has been found to correlate closely with the size of the cadmium hydroxide crystals produced at the end of discharge, large crystals being difficult to reduce (170). Data on crystal size distribution are not available.

Hydrogen evolution has been greatest after discharge at high temperature and low rates (141, 58, 107). This behavior can be interpreted from the characteristic voltage overshoot observed on the cadmium negative electrode at the start of charge (45, 142). The amount of exposed cadmium is small, providing few sites for nucleation, making the local current density high, producing a high over-potential, and as a consequence generating hydrogen gas. Hydrogen gassing at the start of charge can be avoided by starting the charge at a low rate, especially if the preceding discharges were at a high temperature or at a relatively low rate (107).

#### Hydrogen Generation From the Nickel Substrate and Header

Hydrogen does not normally evolve from negative active material during charge because cadmium has a high hydrogen overvoltage. However, the nickel substrate has a much lower hydrogen overvoltage (50), so any exposed substrate or plaque can be a source of hydrogen gassing. Freshly generated nickel on a cadmium negative will gas readily, suggesting that hydrogen could be generated immediately after vibration that opens fresh cracks in the electrode.

Aerospace cells contain metals other than nickel, especially in the header. It would be informative to determine the hydrogen overvoltage of these materials, which include nickel-plated steel, steel cases with and without passivation treatment, steel-to-steel weldments, steel to nickel-plated steel weldments, and brazed joints. Iron, for example, has a lower hydrogen overvoltage at low current than does nickel (143).

### Hydrogen Generation Near End of Charge

Overpotential increases near the end of charge as less  $\text{Cd}(\text{OH})_2$  is left to be charged. If the charge current is still high at this time, or if the  $\text{Cd}(\text{OH})_2$  crystals are large, then the overpotential can be high enough to support hydrogen gassing. Large crystals are particularly harmful because they have low surface area for reaction. Large crystals can be created by a previous discharge at a high temperature, by a discharge at low rate, or by long period of open circuit stand (141, 58, 107). The cadmium electrode voltage becomes more negative under such charge conditions, as seen in Fig. 5-4, promoting hydrogen generation. After the nickel positive electrode is charged enough to generate oxygen gas, the oxygen recombines on the cadmium electrode, causing its potential to be less negative, and stopping the generation of hydrogen there.

If charge of a cell is stopped before hydrogen gassing occurs, then the cell capacity will be less than usual. This lower capacity is generally referred to as hydrogen free charge (142) but it has also been called hydrogen-free capacity (143), charge acceptance (144, 107), and low potential charging capacity (58). The hydrogen-free charge is highest if the charge rate is low, if the prior discharge temperature was not hotter than the charge temperature, and if the prior discharge was at a high rate (Fig.'s 5-5 and 5-6).

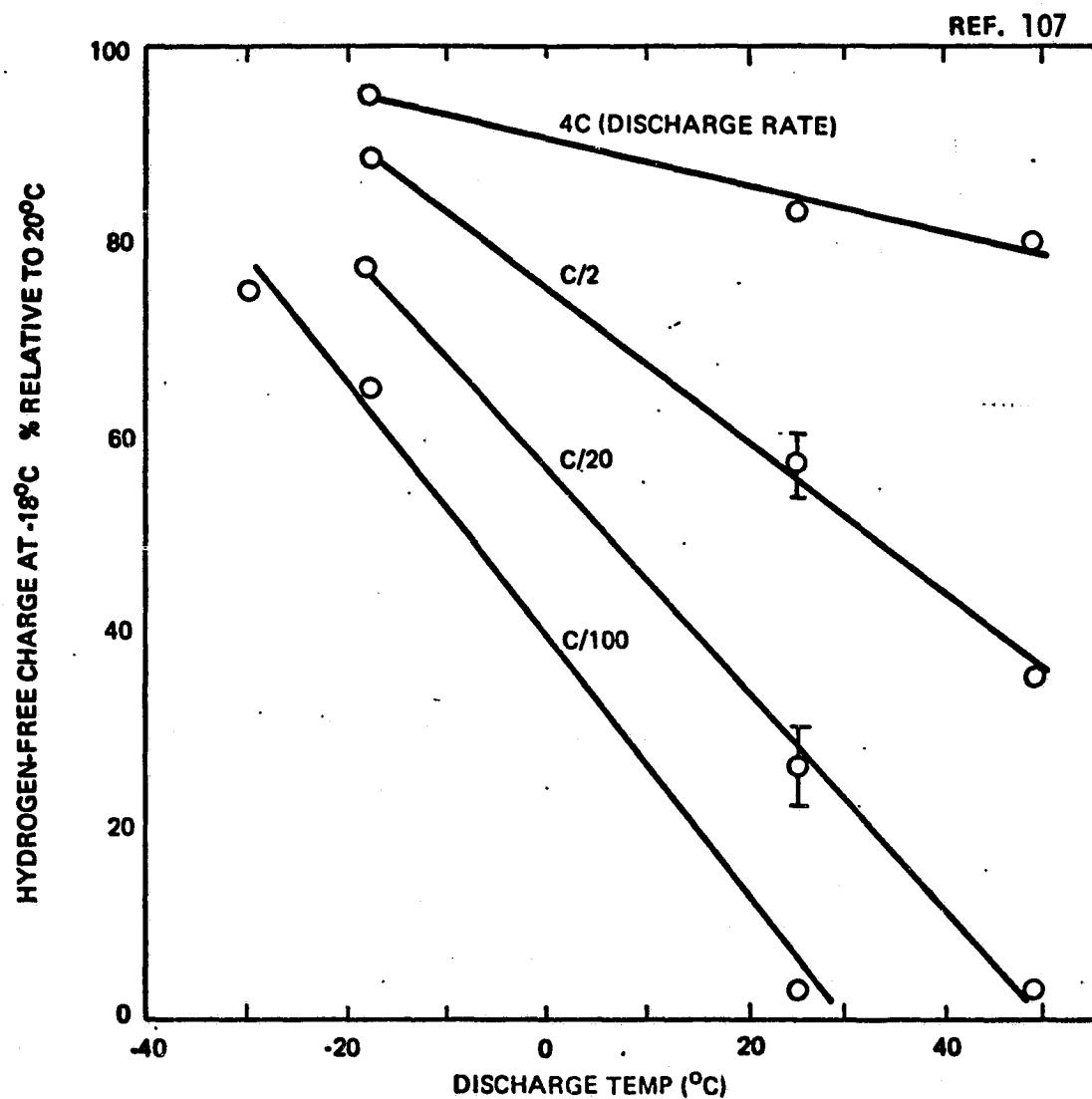
### Hydrogen Generation During Radiation

Radiation with gamma rays to a  $6 \times 10^7$  rad level produces radiolysis of water, releasing hydroxyl radicals that are subsequently reduced by the cadmium, releasing hydrogen (145). Protons having energies of 60 and 137 MeV have had practically no detectable effect on hydrogen generation (146).

### Prevention of Hydrogen Generation

The hydrogen-free charge is lowest at low temperatures and high charge currents (141, 144, 58, 107). Clearly, high charge voltages, high charge currents, or especially low temperatures should be avoided to minimize hydrogen gassing. High voltage, a likely problem with large cells, appears not to have received much attention in cell development. Also, since cells can become negative limited after a long period of charge-discharge cycling, it is worthwhile in spacecraft to be able to reduce the charge rate or charge voltage by ground command to prevent hydrogen generation.





**Figure 5-5. Hydrogen-Free Charge of Cadmium Hydroxide Electrodes at  $-18^{\circ}\text{C}$  at  $C/2$  After Discharging at Various Rates and Temperatures**

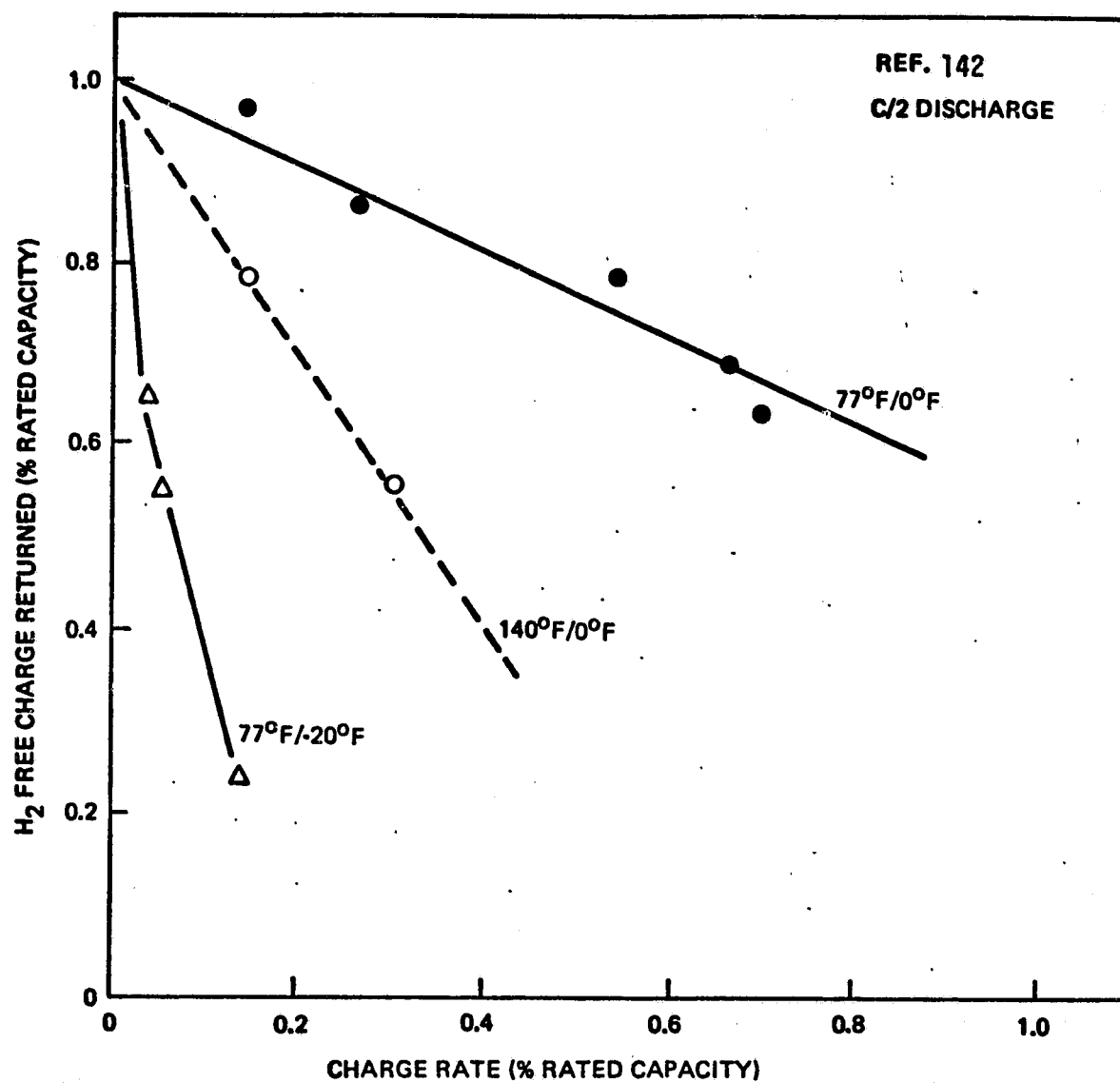


Figure 5-6. H<sub>2</sub> Free Charge Returned vs Charge Rate for Various Preconditioning Temperatures/Charge Temperatures

To avoid hydrogen gassing, the negative plate is usually designed with an excess of uncharged active material so that the positive electrode will evolve oxygen before the negative plate is fully charged. The remaining uncharged negative plate consists of both electrochemically available and unavailable material. The electrochemically available uncharged negative material is what prevents hydrogen gassing by achieving low local current density. Since this material has to be a source of oxygen to the reaction, any oxidation within the cell will reduce the amount of electrochemically available uncharged negative material, reducing the overcharge protection. Corrosion of the nickel positive plate and oxidation of the separator are the two most important oxygen consumers. Leakage of oxygen gas from the cell has the same effect, and the establishment of high oxygen pressure within the cell also takes away oxygen that would otherwise be available for chemical reactions. Special problems are posed during charge of cells that have been idle, for when idle the negative electrode passivates and hydrogen thus evolves more readily.

Charging at low temperature, especially following discharge at a higher temperature, promotes hydrogen generation for several reasons. First, large cadmium hydroxide crystals are formed from the high temperature discharge, as previously discussed. Second, at low temperatures, the nickel electrode is less likely to generate oxygen so the negative electrode is deprived of oxygen for the recombination needed to lower voltage below the hydrogen potential. Third, beta cadmium hydroxide, left in the cell from prior operations at higher temperature, has lower charge acceptance than the gamma form generated during stabilized operations at low temperature (107). Fourth, the greater impedance at low temperature causes the cadmium electrode to be increasingly negative.

One design approach that can avoid many of the hydrogen gassing problems is pre-coating the nickel sinter in the negative plate with a substrate of either silver or cadmium. Silver provides about 0.3 volt of extra over-voltage above that of nickel, and a cadmium substrate would give an additional 0.05 volt of overvoltage protection (50). Use of a cadmium substrate is the design approach adopted in the development of negative-limited nickel cadmium cells (39, 50, 95, 147).

## 6.0 OXYGEN RECOMBINATION

Sealed nickel cadmium cells can be designed so that no gases are evolved, or so that the gases are consumed within the cells as they are produced. Some experimental negative-limited sealed nickel cadmium cells evolve little gas. However, conventional sealed nickel-cadmium cells, the subject of this section, are designed to consume gases as they are produced. The ability to accept continuous overcharge without damage is a key to nickel-cadmium cell design, and has made sealed cells possible. Discovery of this approach was first reported in 1938 (148).

Ideally, oxygen gas evolved from the nickel positive electrode will go directly across the separator and combine on the adjacent negative plate. Reasons why this does not always happen are non-uniformity in the separator, non-uniform gassing in the positive plates because of voltage gradients, non-uniformity in the negative plates, too little or too much electrolyte in the cells, and too much active material loading in the negative plates. In some aerospace cell designs, for example, oxygen recombination occurs primarily at the edges of the negative plates, an undesirable phenomenon. In other cell designs, especially with polypropylene separators, erratic recombination behavior has been caused by intermittent flooding of the separator and negative plates. Some aerospace cells will barely sustain a C/60 overcharge rate at room temperature, whereas cells particularly designed to promote oxygen recombination have operated at their C rate in continuous overcharge, yet generating a gas pressure of less than one atmosphere.

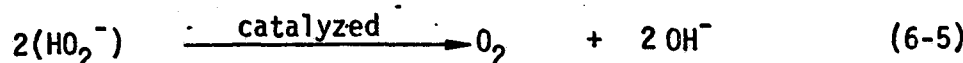
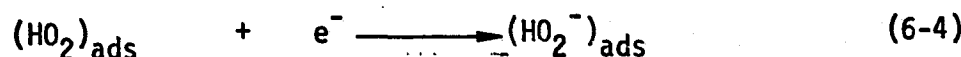
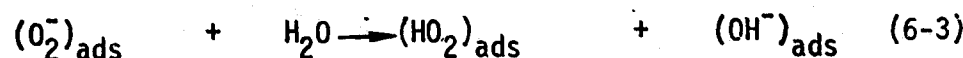
## Chemical Reactions

Early nickel-cadmium battery technologists believed that oxygen recombination occurs by oxygen reacting chemically with cadmium to form cadmium hydroxide, which then electrochemically reduces to cadmium. This mechanism is now considered to be unlikely (46), for experiments have shown the reaction to be electrochemical, and have demonstrated that oxygen can be reduced just as well on nickel as it can on cadmium, provided there is a source of current.

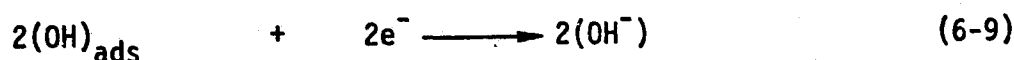
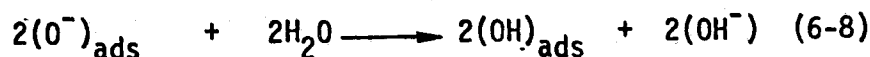
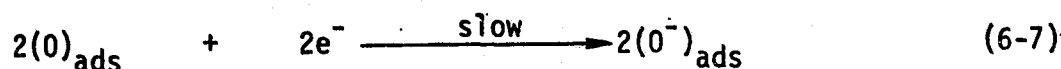
Two parallel paths for oxygen reduction are now known, one involving a peroxide intermediary, and one that leads more directly to hydroxyl ions (149). Oxygen is adsorbed on the surface, and the path followed depends on whether or not the molecule splits into two atoms before combining with an electron. The reactions are as follows\*:



Path 1:

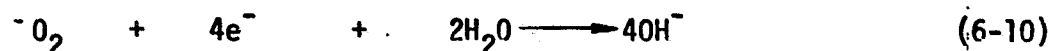


Path 2:



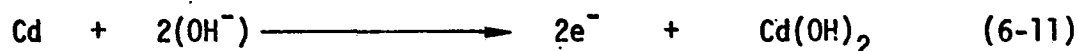
\* Private communication, James Hoare

It will be observed that the oxygen formed in reaction (6-5) goes through the reaction chain again. The overall reaction for oxygen recombination is:



Data are not available to establish which of the two paths is the more important. Silver added to the cadmium electrode will speed oxygen recombination (35), and silver is known to be a good catalyst for decomposition of peroxide, suggesting that path 1 is the predominant one. With oxygen reduction on platinum, impurities in the system have been found to increase the proportion of the peroxide reaction. Thus, impurities might also affect oxygen reduction on the cadmium electrode.

The electrons required for the above reactions are normally provided by the overcharge current. During open circuit, the electrons are provided by oxidation of cadmium metal to cadmium hydroxide,



The cadmium formed during open circuit is reported to be of "lower activity" than that formed by a conventional discharge (150). Substantiating data are not available, however.

The parasitic reaction occurring simultaneously at the positive electrode is:



The oxygen and water generated at the nickel positive electrode must diffuse to the cadmium negative electrode, while hydroxyl ions generated at the cadmium negative electrode must diffuse to the nickel positive electrode. Thus, during both charge and overcharge, the potassium hydroxide at the negative electrode is more concentrated than at the positive electrode, a condition that is reversed during discharge. The current source for equation 6-10 must be either the overcharge current or current obtained from the oxidation of cadmium to cadmium hydroxide. When the cell is open circuited or discharged, oxidation is the only source of current available.

One important effect of the oxygen recombination reaction is that it makes the negative potential move in the anodic (discharge) direction. This is the direct result of the reaction given in equation 6-10. The effect of this voltage reduction is easily observed on cell potential during charge. Conversely, cells with poor recombination capability show a higher transient voltage prior to steady state overcharge because recombination is delayed until the pressure rises.

The major steps in oxygen recombination which will next be discussed in detail are:

1. Absorption of oxygen from the positive electrode into the adjacent liquid KOH.
2. Bulk transport of gaseous oxygen from the positive electrode to a pore in the negative electrode.
3. Absorption of gaseous oxygen into the KOH electrolyte.
4. Diffusion of dissolved oxygen to the reaction site.
5. Diffusion of hydroxyl ions away from the reaction site.
6. Reduction of dissolved oxygen at metallic cadmium, requiring more than one reaction step.

#### Absorption of Oxygen From Positive Electrode To Adjacent KOH

Some of the oxygen evolved from the positive electrode flows as a gas to the cadmium electrode, and the rest is transported by liquid diffusion all the way from the positive electrode. During oxygen generation the layer of KOH next to the positive electrode becomes highly supersaturated, with steady state values 10 to 40 times greater than the equilibrium concentration of oxygen. This apparently is a condition of oxygen bubble formation, and calculations show that in spite of this high initial concentration, the liquid phase transport path contributes less to recombination than does the gas phase path (151).

#### Transport of Gaseous Oxygen

Transport of oxygen in the gaseous phase generally encounters negligible resistance because only oxygen and a little water vapor are usually the only gases present in the cell. Nonuniformities in the separator would not be expected to affect gas-phase transport significantly. Some resistance would occur if the

oxygen had to diffuse through helium, nitrogen or other gases which could concentrate within pores of the negative electrode. However, nitrogen introduced into a cell at various pressures was found to have no effect on the gas recombination rate (127). Apparently, this added element of impedance is much less significant than oxygen diffusion through the liquid KOH.

#### Absorption of Oxygen Into Electrolyte

The gaseous oxygen, after traversing the separator and contacting the electrolyte film on the cadmium electrode, must be absorbed into the electrolyte. No studies are reported on the extent to which gas absorption limits the gas recombination rate, but this is believed to be a relatively small resistance element in the overall process, and the concentration of dissolved oxygen at the gas-liquid interface is expected to be close to saturation. The rate of oxygen absorption into the electrolyte per unit area is:

- a) proportional to the oxygen gas diffusion coefficient; this is proportional to the  $3/2$  power of the absolute temperature and is directly proportional to the absolute pressure (153).
- b) proportional to the oxygen concentration difference between the gas phase and the liquid phase. Since the liquid phase oxygen concentration is low, it may be neglected in an approximation; hence the rate of oxygen absorption would be proportional to oxygen gas pressure.

Since oxygen pressure affects both factors, the rate of gas absorption in liquid KOH should be approximately proportional to the square of the pressure. Experiments show that the recombination rate is approximately proportional to the pressure to the first power (152), so the oxygen absorption step does not control and is indeed a relatively small resistance element in the overall recombination process.

The amount of oxygen that can dissolve is normally limited by the equilibrium solubility of oxygen in KOH. The equilibrium solubility of oxygen decreases with increasing concentration of KOH, and is only slightly affected by temperature with 30% KOH (57). Although as previously discussed, considerable supersaturation of oxygen in KOH occurs immediately adjacent to the positive electrode as a condition of oxygen bubble formation, supersaturation would not be expected in the liquid film adjacent to the cadmium electrode.



### Diffusion of Oxygen to the Reaction Site

The next step, diffusion of dissolved oxygen to the reaction site, is a significant resistance element in the gas recombination process. The mass transfer rate per unit area for this step is:

- a) proportional to the liquid diffusion coefficient, which is relatively insensitive to oxygen pressure, but increases a little with increasing temperature, and decreases a little with increasing KOH concentration (154).
- b) proportional to the oxygen concentration difference across the liquid film; during recombination this driving force should be roughly proportional to the solubility of oxygen in KOH, which decreases with increasing KOH concentration, and is practically unaffected by temperature at 30% KOH concentration (57).
- c) inversely proportional to the liquid film thickness.

It may be noted that temperature per se is not predicted to be a major factor in this rate-limiting step. This was confirmed by carefully controlled experiments in which variables other than temperature were held nearly constant (141). Temperature does have some affect in the overall recombination process, however, for it is well known that cells develop higher pressure at low temperature than at high temperature, as shown in Figure 6-1 from Reference 127.

Calculations show that the diffusion distance must be very short to sustain high recombination rates (45). For example, for the gas pressure within the cell not to exceed one atmosphere at a C/10 continuous overcharge rate, the diffusion layer would have to be thinner than 0.0001 inch, which is only 3 percent of typical plate separation and 30 percent of the average pore diameter. Theoretical and experimental evidence shows that the films obtained with fuel cell technology are about one micron thick (155), and calculations on an experimental cadmium electrode showed the film thickness to be 0.4 micron (151). Nevertheless, such performance is seldom obtained in nickel cadmium cells, probably because the pores are so small that they become flooded (133). Flooding occurs because surface tension effects become stronger as pore size decreases. Flooding, for a given amount of electrolyte,

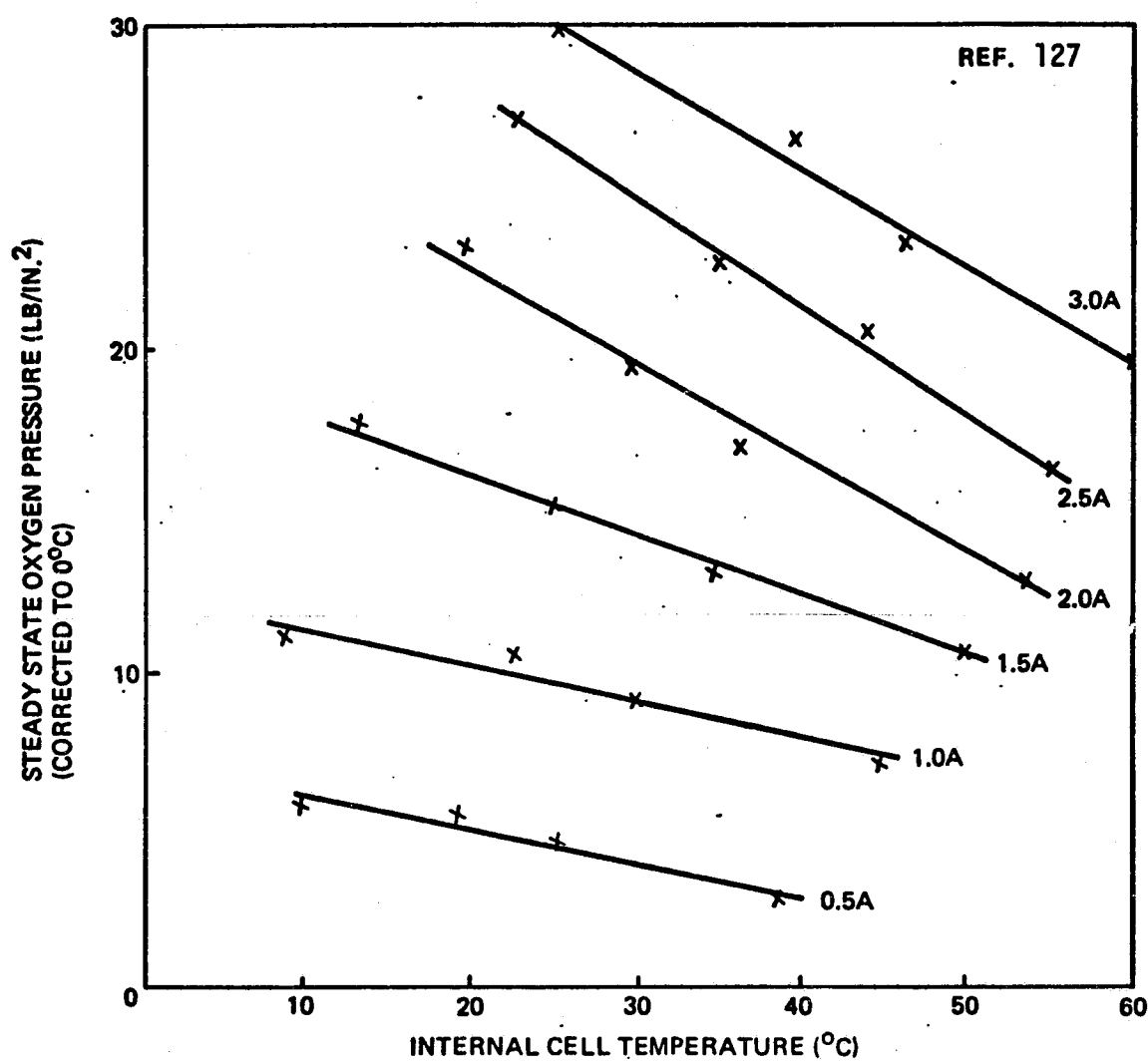


Figure 6-1. Effect of Temperature on Recombination in a 4 A-hr Cell With Impregnated Negative Plates

can be prevented by designing the negative plate with sufficiently large pores. However, the most important factor in controlling diffusion thickness is the amount of electrolyte in the cell. Figure 6-2 from reference 127 shows that the diffusion thickness increases substantially with the addition of electrolyte. In this illustration diffusion thickness was calculated from test data, and is expressed as the term  $d/ASD$  where  $d$  is diffusion thickness,  $A$  is area of the recombination reaction,  $S$  is solubility of oxygen in moles/cm<sup>3</sup>-atm, and  $D$  is the oxygen diffusion constant in cm<sup>2</sup>/sec.

#### Diffusion of Hydroxyl Ions Away From Reaction Site

While oxygen is diffusing through the liquid film and reacting at the negative electrode, water is also being consumed in the reaction, with the generated hydroxyl ions diffusing away from the site. From equations 3-1 and 6-10, it is seen that for both charge and overcharge each electron transferred results in one hydroxyl ion. Since the overcharge rate is usually much lower than the charge rates, fewer hydroxyl ions must migrate during overcharge than during charge, and thus should diffuse readily. A difficulty, however, is the fact that only cadmium sites associated with relatively thin electrolyte films can participate significantly in recombination, whereas even the flooded sites can readily charge and discharge. This limitation on participating sites increases electrolyte concentration, slows down recombination, and also affects other cell characteristics due to higher solubility of cadmium species at high KOH concentration. This aspect of oxygen recombination does not appear to have been studied.

#### Reduction of Dissolved Oxygen at the Metallic Cadmium Surface

Reaction of dissolved oxygen with cadmium at the metallic surface is the final step in the recombination process. This reaction has been found to be electrochemical rather than chemical (156), during both overcharge and open circuit, as indicated by the change of the oxygen reduction rate with the potential of the negative electrode (135). The test data do suggest, however, that perhaps a small part of the recombination process is chemical rather than electrochemical, but the chemical process is not of any great significance (157).

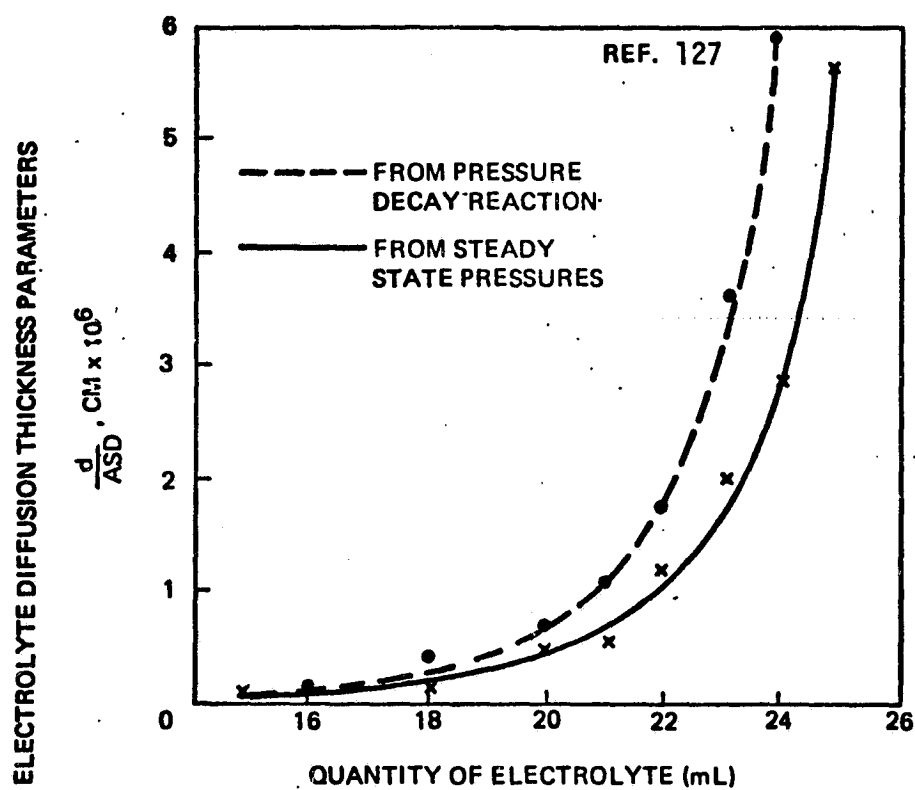


Figure 6-2. Variation of the Thickness of Electrolyte Layer With Quantity of Electrolyte

Experimenters seeking to understand the oxygen recombination process have recognized the importance of the three-phase boundary in providing suitable area for the reaction. They found that in a given configuration, the following factors were the most important:

- 1) The area of exposed metal. A nickel plaque will perform nearly as well as a cadmium electrode.
- 2) The potential of the negative electrode. Increasing the potential in the charge direction (more negative) increases the gas recombination rate.

Experimental results from reference 135, shown in Figures 6-3 to 6-6, illustrate these findings. The experiments were conducted in such a way that the negative electrode potential could be varied, and the equilibrium  $\text{Cd}/\text{Cd}(\text{OH})_2$  potential of -0.840 volts measured from a standard hydrogen electrode is the reference point. Figure 6-3 shows the oxygen reduction rate with a nickel plaque, which, if plotted on semi-log paper, would correspond to Tafel lines. When cross-plotted, the oxygen reduction rate is linear with pressure, showing that the process is diffusion limited. This catalytic activity of nickel, incidentally, is the principle used for oxygen pressure sensing with most auxiliary electrodes in nickel cadmium cells.

Figure 6-4 shows similar results for a  $\text{Cd}/\text{Cd}(\text{OH})_2$  electrode constructed with no nickel. At negative potentials performance is quite similar to that of the nickel plaque; at more positive potentials the cadmium metal is nearly completely oxidized to  $\text{Cd}(\text{OH})_2$ , which is a poor conductor. Performance in the range between full charge and full discharge depends on the fraction of metallic cadmium exposed. The performance of a typical cadmium electrode formed on a nickel plaque is shown in Figure 6-5. The oxygen reduction rate can be seen to be intermediate between all-nickel and all-cadmium electrodes, corresponding to about 27% nickel and 73%  $\text{Cd}/\text{Cd}(\text{OH})_2$ . Figure 6-6 shows the oxygen reduction rate plotted versus oxygen pressure, the linear relationship proving that the process is diffusion limited.

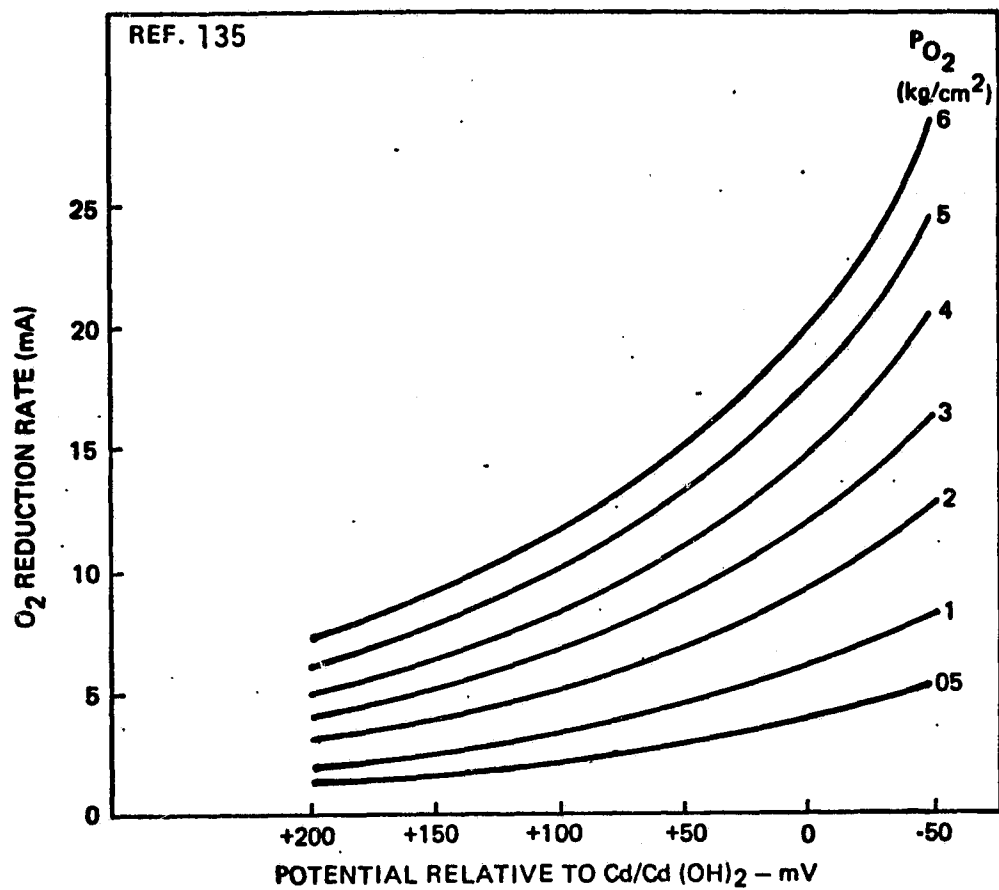


Figure 6-3. Pure Nickel Sintered Cathode Potential Dependence

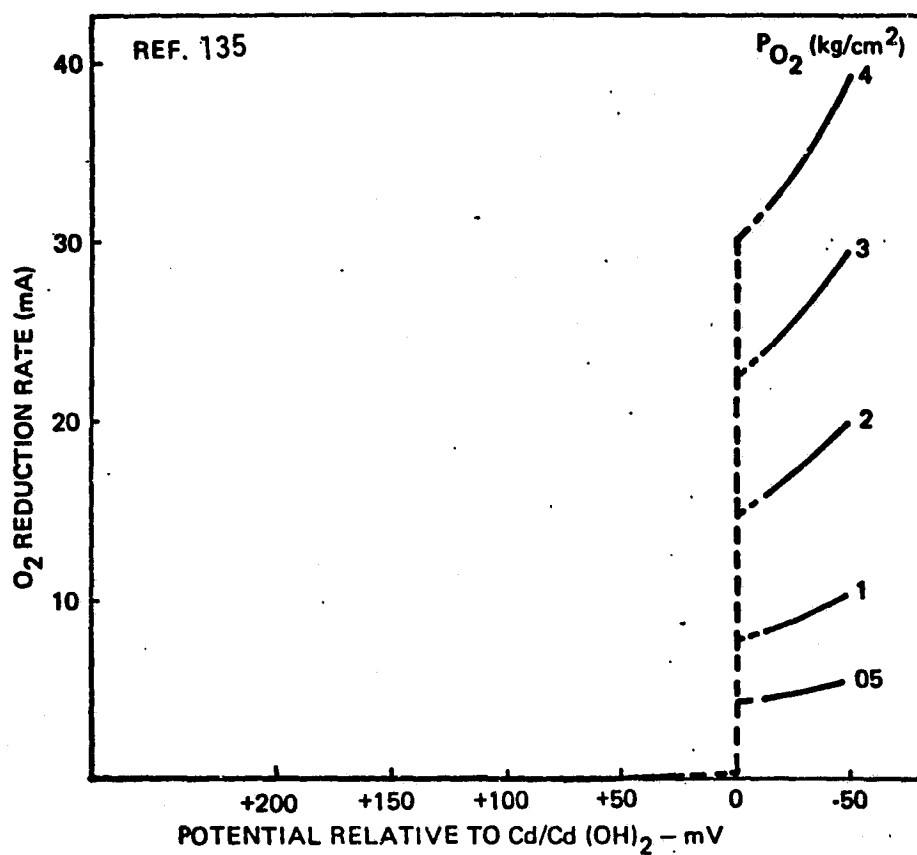


Figure 6-4. Pure Cd-Pressed Cathode Potential Dependence

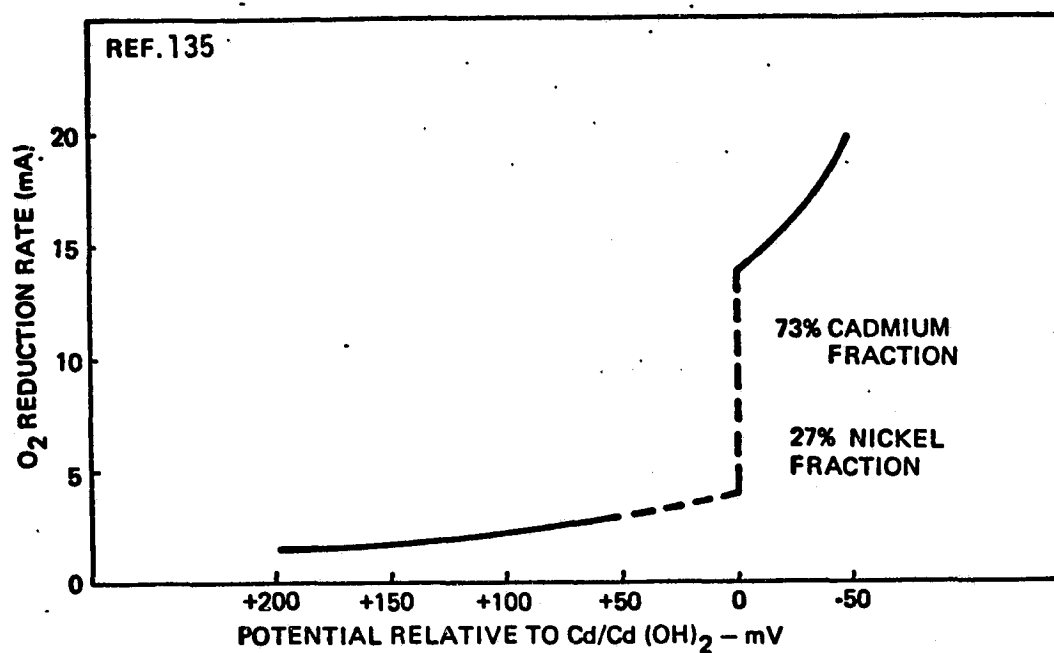


Figure 6-5. Cd-Impregnated Ni-Sintered Cathode Potential Dependence



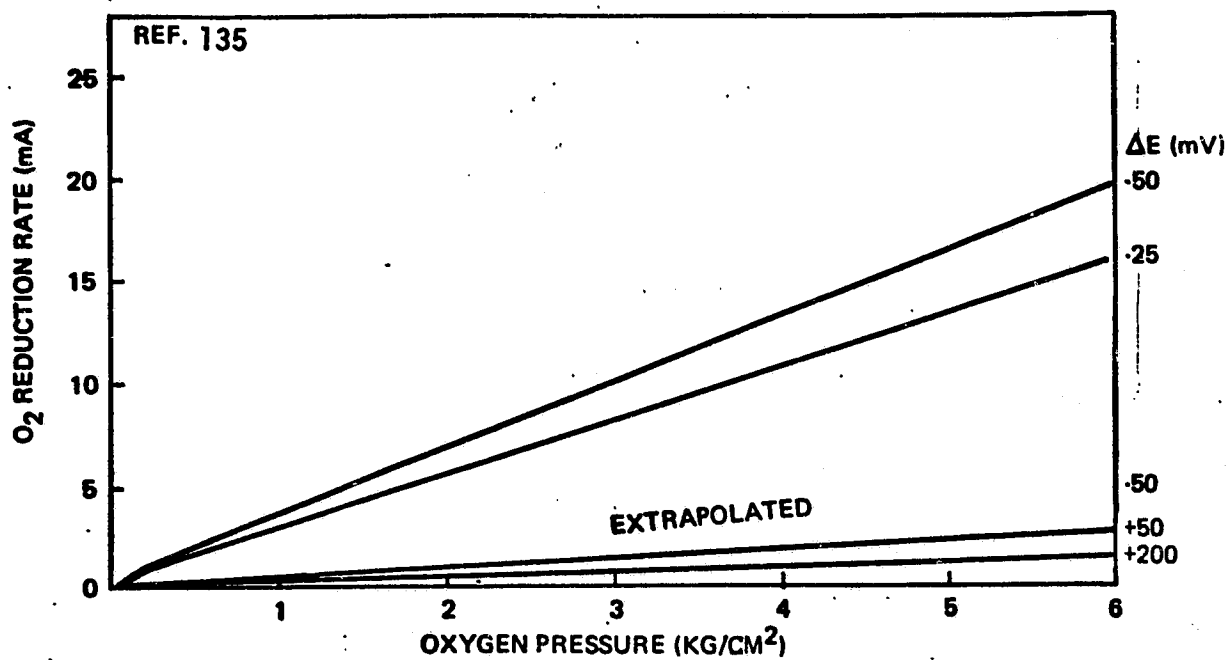


Figure 6-6. Cd-Impregnated Ni-Sintered Cathode Pressure Dependence

Because oxygen recombination occurs primarily at metallic cadmium sites, it is helpful to have much exposed cadmium metal. This can be achieved by increasing the state-of-charge of the cadmium electrode, as demonstrated by steady state pressure measurements, and by analysis of pressure decay rates (152). Figure 6-7 from reference 152 shows the recombination rate parameter plotted as a function of cell state-of-charge, expressed as the ratio of metallic cadmium on the negative electrode to active nickel on the positive electrode. In another experiment comparing two states of charge, however, pressure decay data showed that the amount of excess metallic cadmium at full charge did not have a significant effect of the reaction kinetics (133). Other findings of interest from reference 152 tests were:

- 1) Increasing the state-of-charge resulted in higher cell voltages and presumably higher cadmium electrode potentials. This probably is caused by increased polarization associated with reducing the amount of  $\text{Cd(OH)}_2$ .
- 2) Prior state-of-charge history affected the steady state pressure, with higher pressure occurring when the amount of cadmium metal had previously been low. Changes in the three-phase boundary are probably the cause of this.
- 3) Changes that occur within cells can have a temporary effect on the recombination rate. For example, the first charge cycle of a series can have high oxygen pressure, and long continuous overcharge can cause a gradual lowering of pressure. These effects are probably caused by a redistribution of active cadmium metal, and possibly also by changes in the three-phase boundary.
- 4) The recombination-rate constant calculated during pressure decay is non-varying except at low pressures, where a decrease is noted. Presumably near the end of the decay the diffusion path is increased as nearby cadmium metal becomes depleted and more distant material is reacted with.

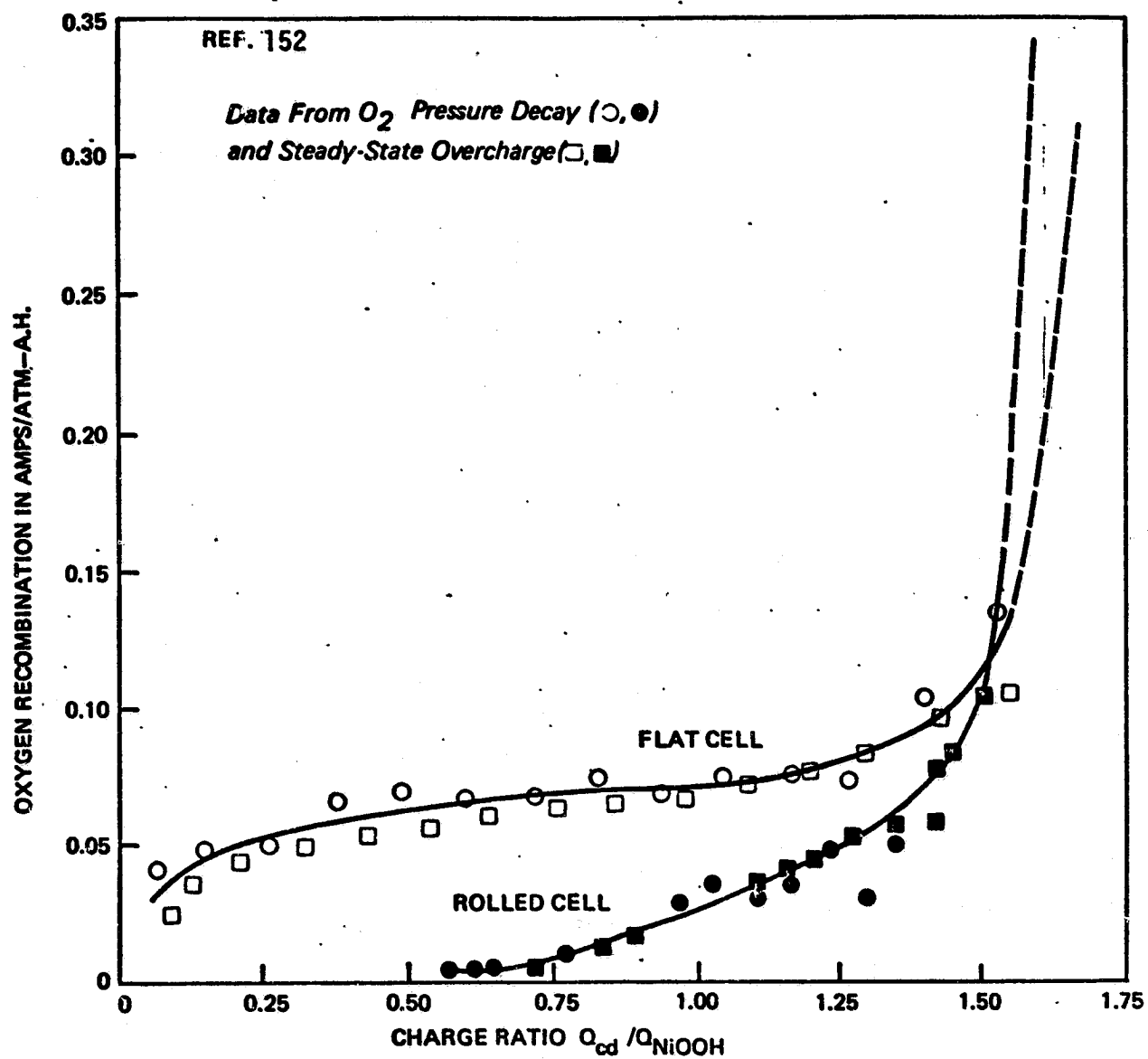


Figure 6-7. Oxygen Recombination Rate versus Cadmium Electrode State-of-Charge

Although oxygen combination occurs primarily at metallic sites, it also occurs to some degree on  $\text{Cd}(\text{OH})_2$  films, as has been demonstrated in film experiments with oxygen-saturated KOH (92).

Silver added to the cadmium electrode has been found to increase oxygen recombination significantly (35). The amount needed is very small, less than 0.03% of the total impregnated materials. The fact that silver catalyst improves the recombination rate shows that the reaction kinetics are important, and that oxygen diffusion is not always the rate-determining process. Decomposition of hydrogen peroxide, which silver will quickly do, is believed to be silver's function in accelerating oxygen recombination.

#### Effect of Design Variables

A high state of charge on the negative electrodes, which enhances recombination, can be achieved by providing a large reserve of charged cadmium in the cell design. Figure 6-8 from reference 127 shows that more fully charged plates recombine oxygen best, and also that low amounts of electrolyte enhance gas recombination.

High porosity, attained by light loading, also improves recombination as shown in Figure 6-9 from reference 127. Viewed another way, a high porosity permits more electrolyte for the same cell pressure.

Excess electrolyte lowers the oxygen recombination rate because of added oxygen diffusion resistance. In the intermediate state between well starved and fully flooded, contributions to this added resistance are flooding of electrode pores, thickening of the electrolyte at the separator-electrode interface, and local blockage of passages in the separator. The contribution of each agent has not been precisely determined. The fact that lightly loaded plates with relatively large pore sizes will recombine oxygen at relatively high electrolyte quantity suggests that flooding of electrode pores is the first effect of too much electrolyte.

Separator thickness and the degree to which the separator is compressed does have a small but minor effect on the recombination rate as shown in Figure 6-10 from reference 127. Density and void volume of the separator material

REF. 127

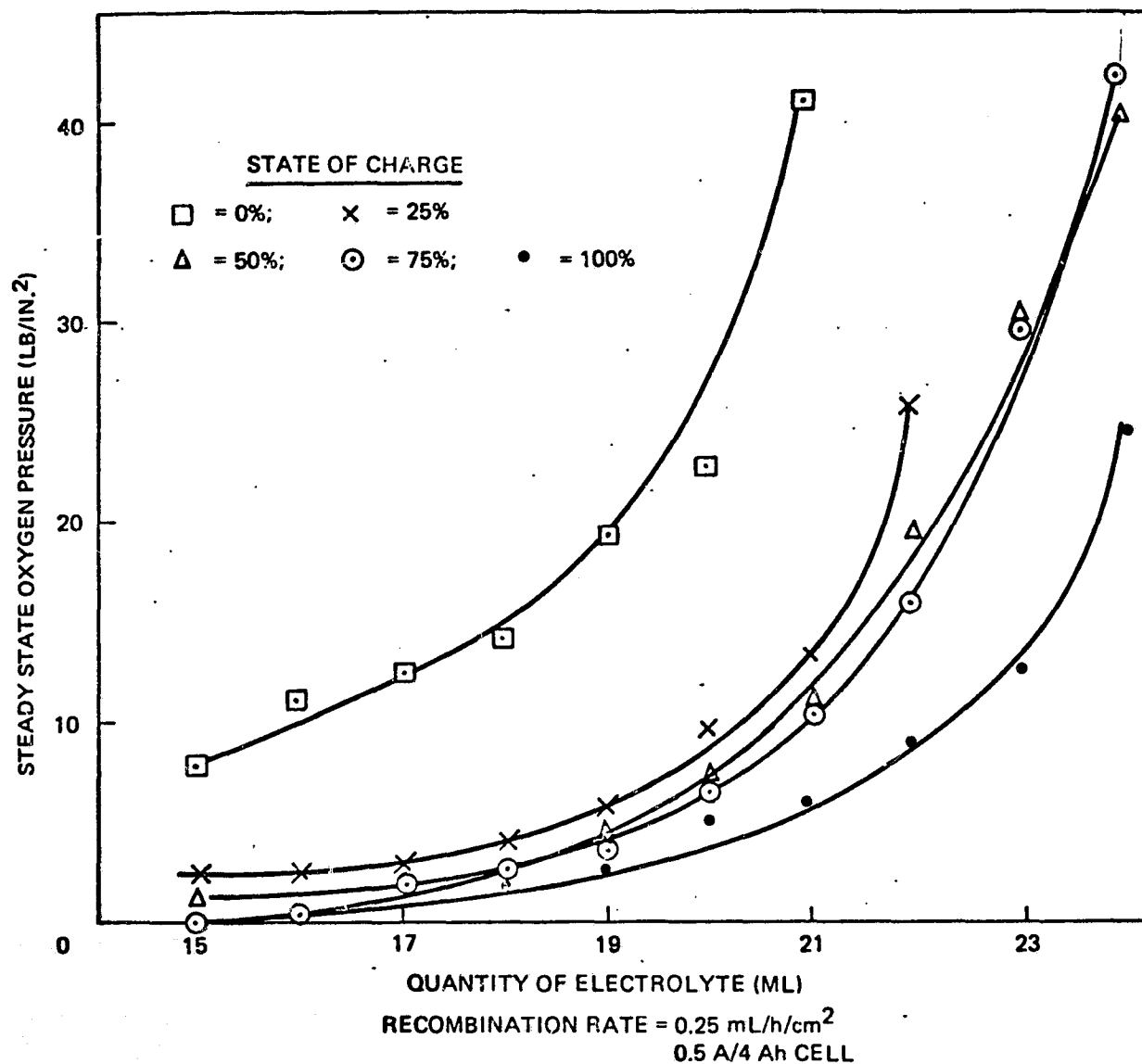


Figure 6-8. Effect of State of Charge of Negative Plates on Recombination Properties of a 4 A-hr Cell

	Cd (g/cm <sup>3</sup> )	PLATE POROSITY (% OF TOTAL VOL)
x	1.06	53
⊙	1.64	47
*	1.90	46

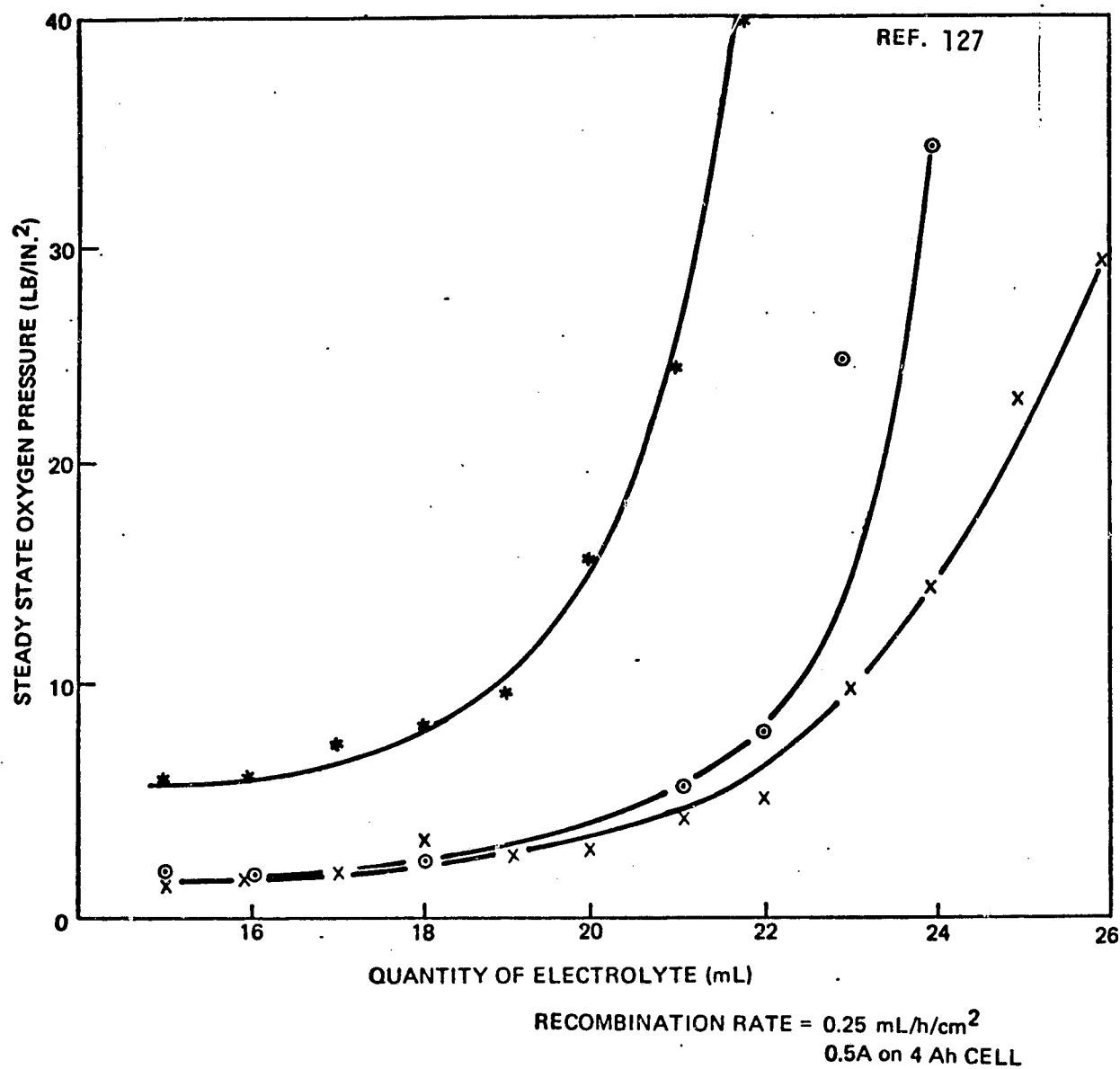


Figure 6-9. The Effect of Porosity on Steady State Pressure

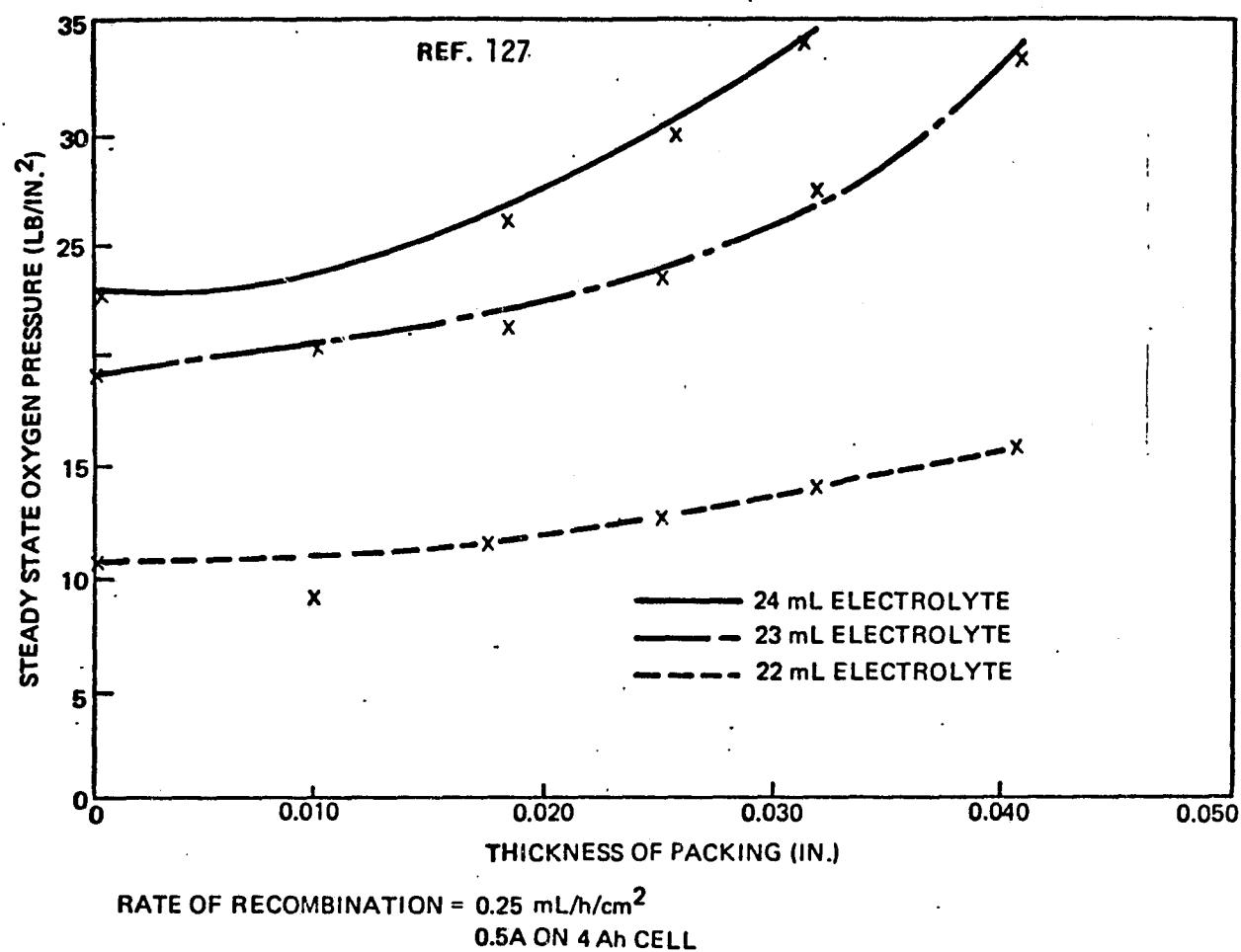


Figure 6-10. Effect of Tightness on Recombination Properties of a 4 A-hr Cell

might have affected the recombination rate, but it is not clear to what degree these variables were changed during this particular test.

Specific gravity also affects recombination rate, as shown in Figure 6-11 from reference 127. The better recombination with dilute KOH (low specific gravity) is likely due to the higher solubility of oxygen (57), and more rapid oxygen diffusion (154).

In a group of tests the potassium hydroxide electrolyte was replaced in one case by an equal concentration of potassium carbonate, and in another by potassium hydroxide saturated with lithium hydroxide (127). These test results were the same as with potassium hydroxide, showing that these materials had no significant short term effect on the kinetics of gas recombination.

Another experiment produced just the opposite results. Adding carbon dioxide gas to a cell lowered the gas pressure during overcharge (161). The mechanism proposed for this improvement in recombination was carbonate ions converting "compact" nonconducting  $\text{Cd}(\text{OH})_2$  to a "non-compact" conducting  $\text{Cd}(\text{OH})_2$ , allowing the entire Cd electrode, rather than just the reduced Cd and exposed Ni sinter, to be effective in reducing  $\text{O}_2$ .

In a third experiment, carbonate was added to cells which when cycled produced lower recombination rates (59). It appears, therefore, that the short term and the long term effects of carbonate can differ. Since the long term effects are generally of greatest importance, it may be concluded that carbonate in cells is not beneficial because it will ultimately reduce recombination rate. This agrees with the claims in Reference 31, although data are not supplied in that reference.

#### Design Considerations Affecting Recombination

The rate of oxygen recombination depends on the amount of cadmium, plus to some degree nickel, surface available, and the rate at which oxygen can diffuse to the metal surfaces. Techniques which will improve recombination in cells are:

- 1) Design a large charge-reserve in the negative electrodes to furnish the needed metallic cadmium surface. This charge reserve should be



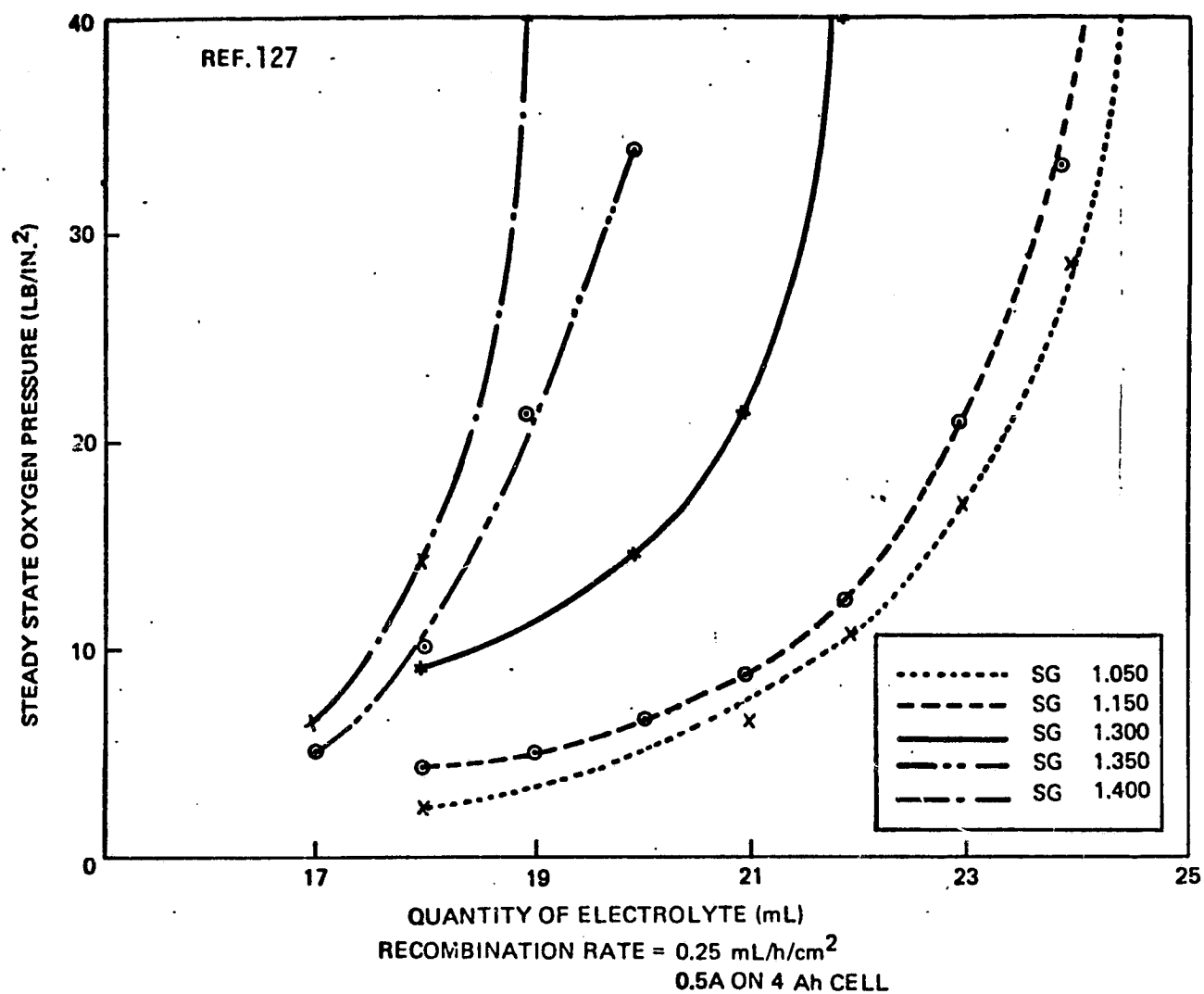


Figure 6-11. Effect of Specific Gravity of Electrolyte on Recombination Properties of a 4 A-hr Cell

- 1) supplied without reducing the amount of cadmium hydroxide because the need for cadmium hydroxide is dictated by other requirements, especially protection against hydrogen generation. Thus, a high negative-to-positive ratio will result from the increased charge reserve.
- 2) Avoid overloading the negative plates (142). Much of the extra cadmium in highly loaded electrodes is not available, and the resulting small pores become flooded with electrolyte, preventing oxygen access. Figure 6-12 shows the effect of loading and electrolyte amount on pressure, and Figure 6-13 shows the low steady-state pressure obtained on the lightly-loaded Bell Telephone labs cells.
- 3) Provide uniform separators having good wetting and wicking capability to assure adequate and uniform electrolyte contact at the negative electrodes.
- 4) Use dimensionally-stable nickel positive electrodes that do not expand with cycling. This minimizes electrolyte migration and helps maintain consistent recombination rates. Electrochemical impregnation, which does not corrode plaques, produces nickel positive electrodes that have better dimensional stability than those made by other processes.
- 5) Provide silver in the negative plates to catalyze oxygen recombination (35). The silver, being at the negative potential, does not oxidize and hence will not migrate. This effective additive is now used in some aerospace cells.
- 6) Provide dispersed Teflon in negative plates to improve oxygen recombination and retard cadmium migration (159). Dispersed Teflon apparently increases the three-phase boundary area and thus improves recombination significantly. Cells having Teflon in negative plates can accept up to 20 percent more electrolyte without excessive pressure, thus reducing the probability of the separators drying-out.
- 7) Rather than design for high recombination capability, design the charge control to a limited overcharge rate. The cell can be designed to produce voltage tailup at the end-of-charge to make end-of-charge easier to detect. Without provision for recombination of oxygen the negative electrode would not exhibit voltage suppression that would otherwise accompany gas recombination, so the voltage rises at end-of-charge.

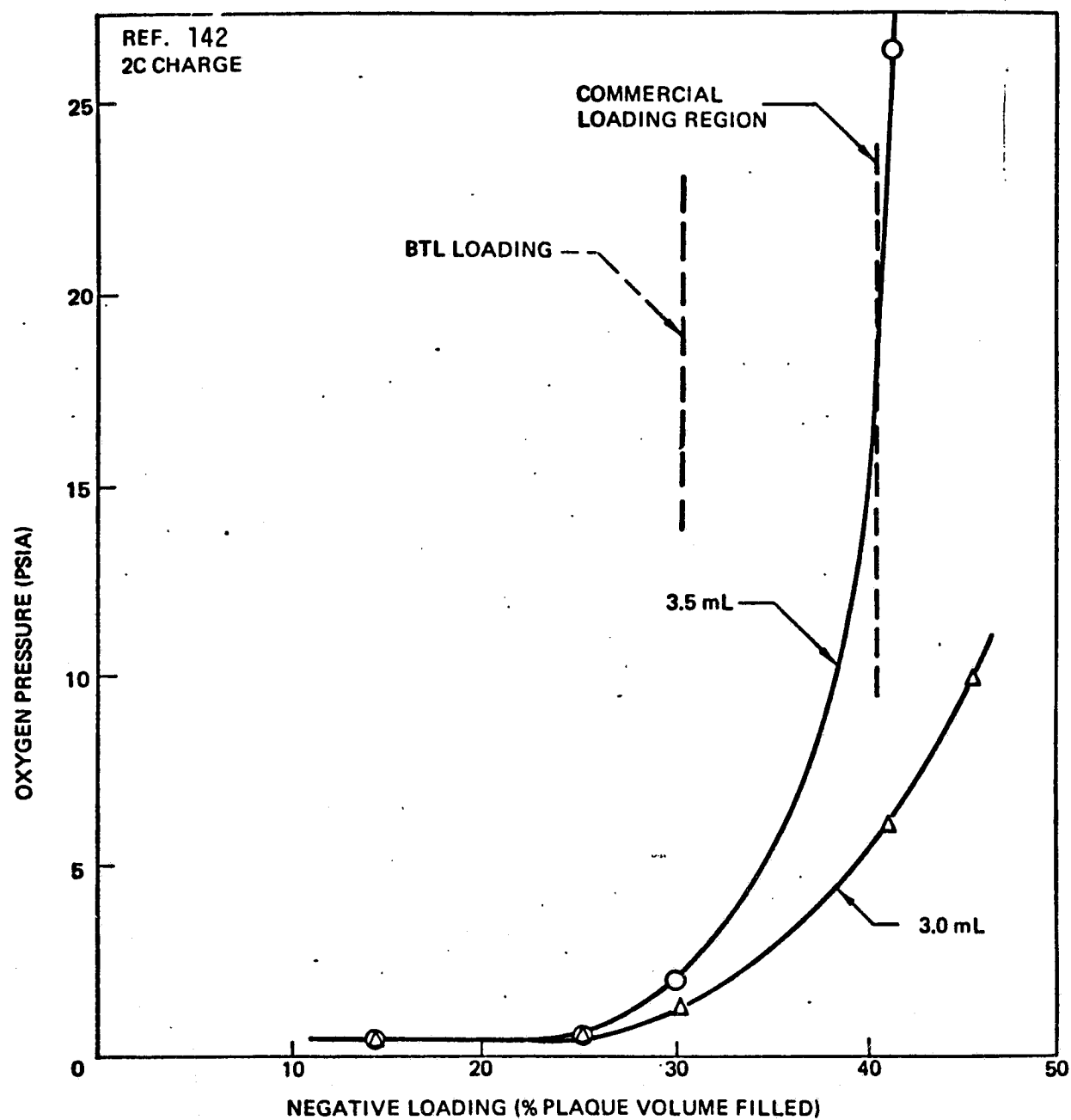


Figure 6-12. Effect of Negative Loading and Quantity of Electrolyte on Steady State Oxygen Pressure

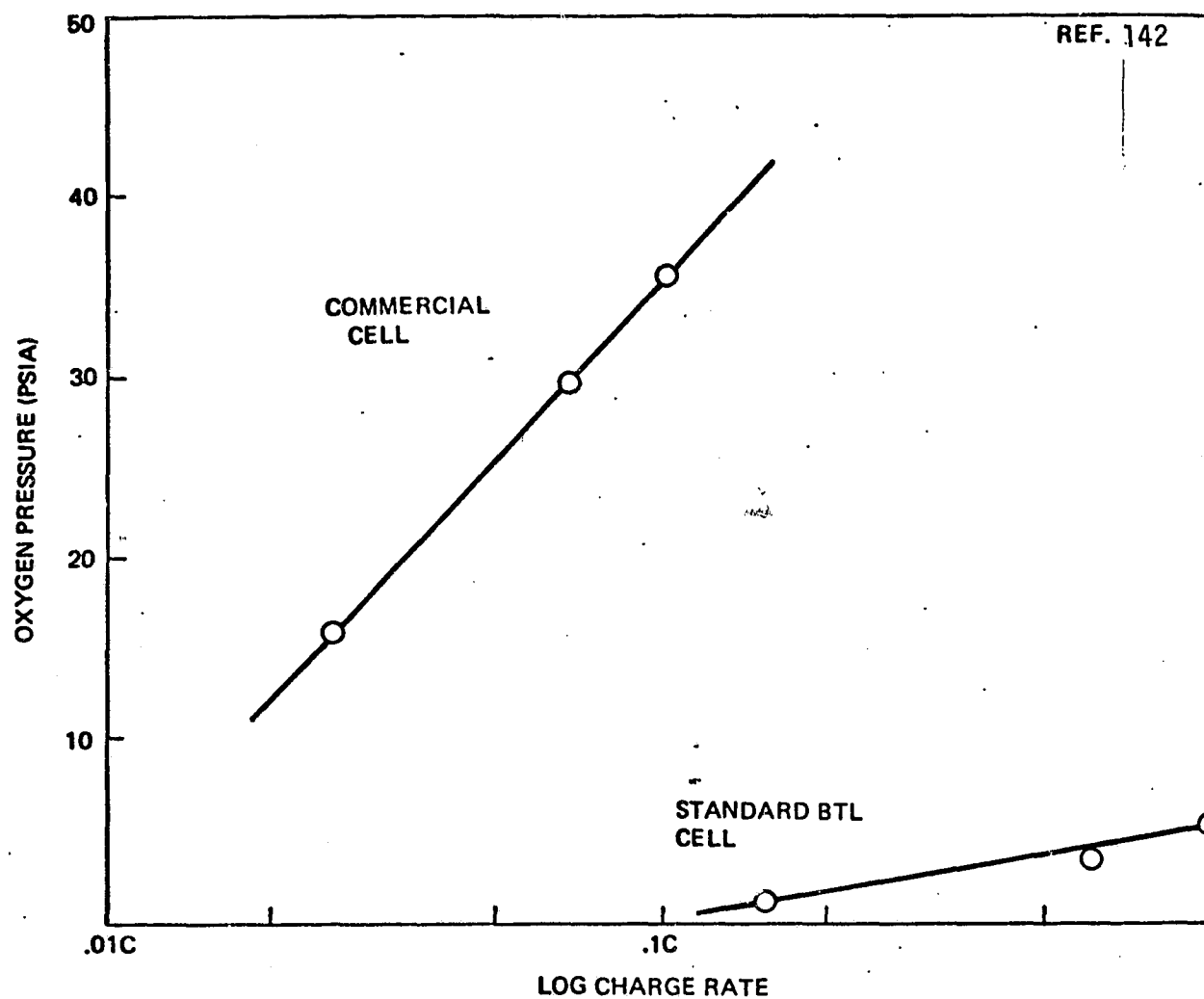


Figure 6-13. - Effect of Charge Rate on Steady State Oxygen Pressure

- 8) Design, manufacture and operate the cells to minimize carbonate accumulation. Carbonates in nickel cadmium cells alter both positive and negative electrodes so as to impede oxygen recombination (31, 59).
- 9) Provide in each cell one or more special plates having high oxygen recombination capability. For example, reference 160 describes a cell with the outermost electrode having 45 to 60% porosity, compared with 25 to 45 percent for the remaining negative plates.

## 7.0 OPERATION AND CYCLING EFFECTS

### Electrode Characterization

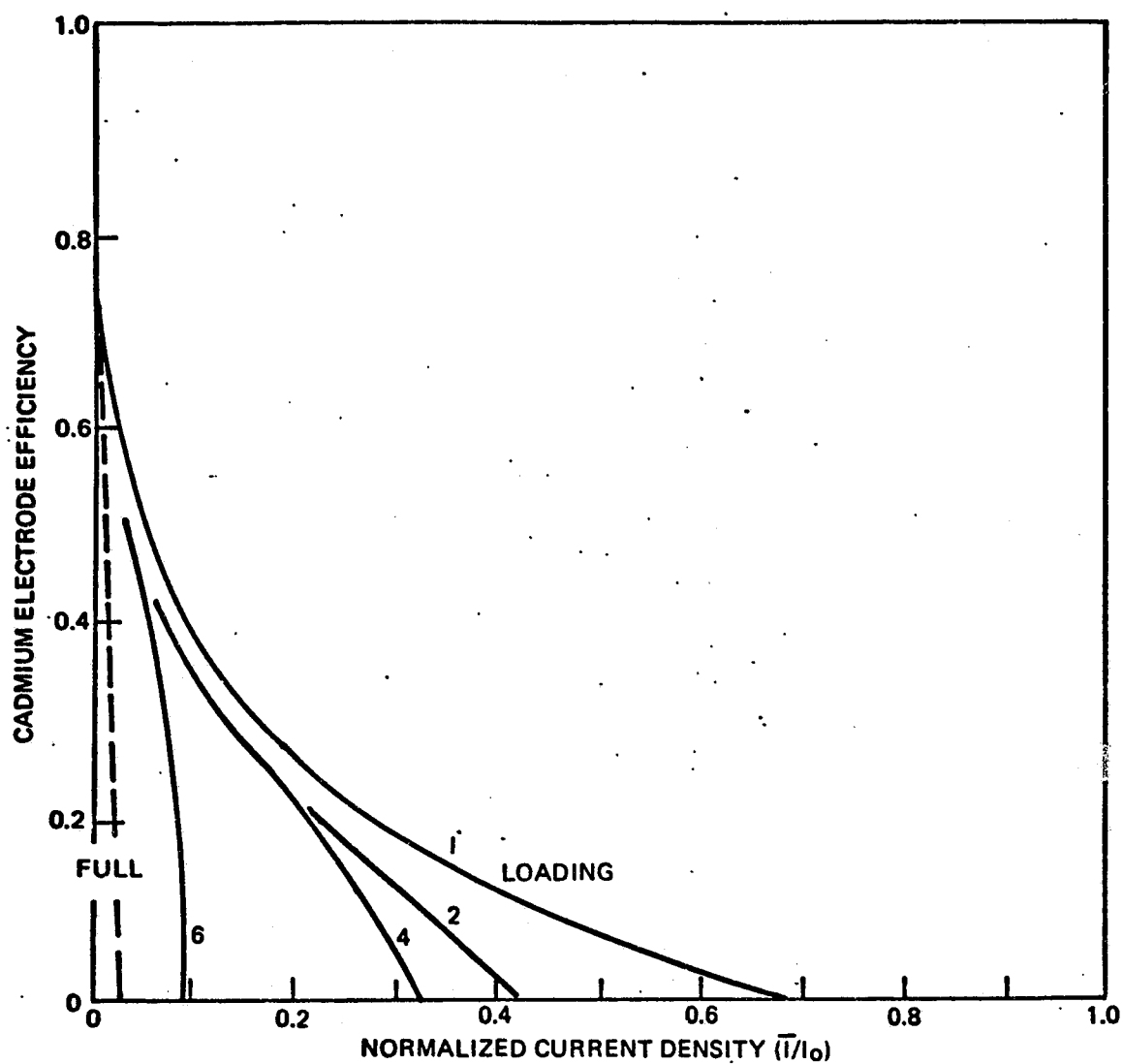
A fundamental cause of difficulties with the cadmium electrode arises from cadmium's metal expansion in volume by a factor of 2.35 when discharged to cadmium hydroxide. The resulting choking of the pores is aggravated as the reaction zone advances during discharge from the exterior to the interior of the electrode with the discharge product obstructing mass transfer. Active material migrating from the interior of the electrode toward the external surface further impairs mass transfer (93, 99).

Evidence for the existence of choking effects is indisputable. A simple calculation (100) shows that if pore geometry were changed during discharge then the limiting current density would be proportional to the free volume to the 3/2 power, whereas experimentally a sixth power relationship is obtained. This power dependence on free volume is so sharp that it can only be explained by the reaction becoming choked off at the necks of the pores. Choking is even evident in photomicrographs (61). Increasing impedance with discharge also supports the pore choking theory (60).

On relatively new electrodes, the pore choking is most pronounced on plates with the highest loadings. When capacity-current curves for different loadings are extrapolated to the point at which the amount of cadmium approaches zero, then a limiting current density of  $1.2 \text{ A/cm}^2$  results with a plaque having a free volume of 89 percent (100). Normalizing discharge current to this limiting value gives efficiency-current curves such as in Fig. 7-1 (100). A choking index is defined by Casey as being the slope of curves such as those in Fig. 7-1, arbitrarily taking the reference point at an efficiency  $\bar{Q} = 0.3$ . These curves also give a basis for estimating the capacity fractions contributed from the plate surface, from the walls of the large pores, and from the buried active material (100).

Another way to define choking is based on the Bruggeman-Baron equation for the electrolyte conductivity of a porous body, thus:

$$K_p = K_s (1-f)^{3/2}$$



BASIS:

$I_0 = 1.25 \text{ A/cm}^2$ , LIMITING CURRENT DENSITY AS IMPREGNATED CADMIUM APPROACHES ZERO  
REF. 100

LOADING DATA—

NO. OF LOADINGS	WEIGHT GAIN Grams	LOADING Ah/cm <sup>2</sup> mm	FREE VOLUME CC PORES/CC PLATE
1	0.5330	0.0057	0.858
2	1.1295	0.0121	0.822
4	2.3578	0.0255	0.747
6	3.8771	0.0414	0.654

Figure 7-1. Effect of Loading on Cadmium Electrode Efficiency

where  $K_p$  = conductivity of porous body  
 $K_s$  = conductivity of solution in pores  
 $f$  = volume fraction of solids in the body

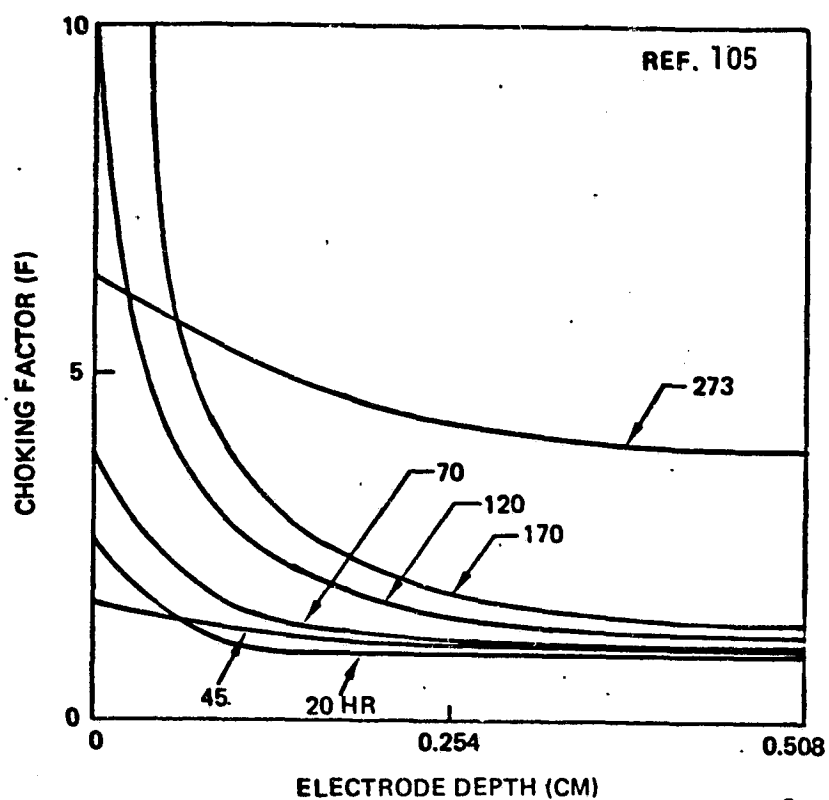
The choking factor is then defined as the ratio of the resistance of the porous body at any time,  $t$ , to the initial resistance, and becomes the ratio of the term  $(1-f)^{3/2}$  at time zero to its value at time  $t$  (105). Using this method, typical choking patterns on thick, experimental electrodes are derived and plotted in Fig. 7-2. They correspond to discharge profiles shown in Fig. 7-3. These choking patterns show how the process starts near the front surface and then gradually moves into the electrode interior. Discharges at low rates can be carried out more completely, and thus produce the greatest degree of choking.

It should be noted that Casey found that the theoretical exponent of  $3/2$  used in the Bruggeman-Baron equation to be too small (100), at least when evaluated at high current density. Use of an exponent greater than  $3/2$  would increase the choking factors shown in Fig. 7-2.

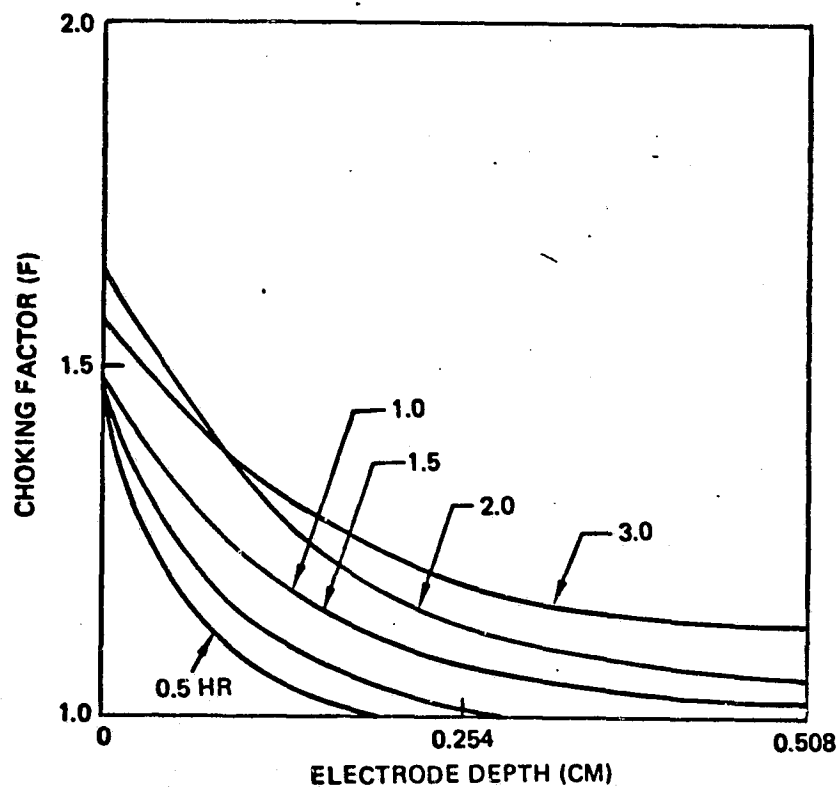
Figs. 7-2 and 7-3 show how during discharge the current wave starts near the front of the electrode and gradually advances into the interior, with choking predominating near the electrode surface. The depth to which the discharge reaction penetrates into the electrode depends on the relative magnitude of the mass transport and Faradaic impedances. This ratio, called the Thiele parameter, is analogous to the throwing capability in electrochemical plating, and is affected by the electrode design, degradation effects, and operating parameters. The Thiele parameter thus measures the ratio of the rate of the surface reaction to the rate of diffusion into the porous structure. A time evolution of the Thiele parameter on a thick experimental electrode (105) is shown in Fig. 7-4. Porosity decreases during discharge, increasing ionic impedance, but the Faradaic impedance increases even more because the front regions of the electrode approach passivation. Thus a decrease in this parameter accompanies more reactivity within the electrode interior as discharge progresses.

The following cell design features reduce choking and promote even discharge throughout the cadmium electrode.



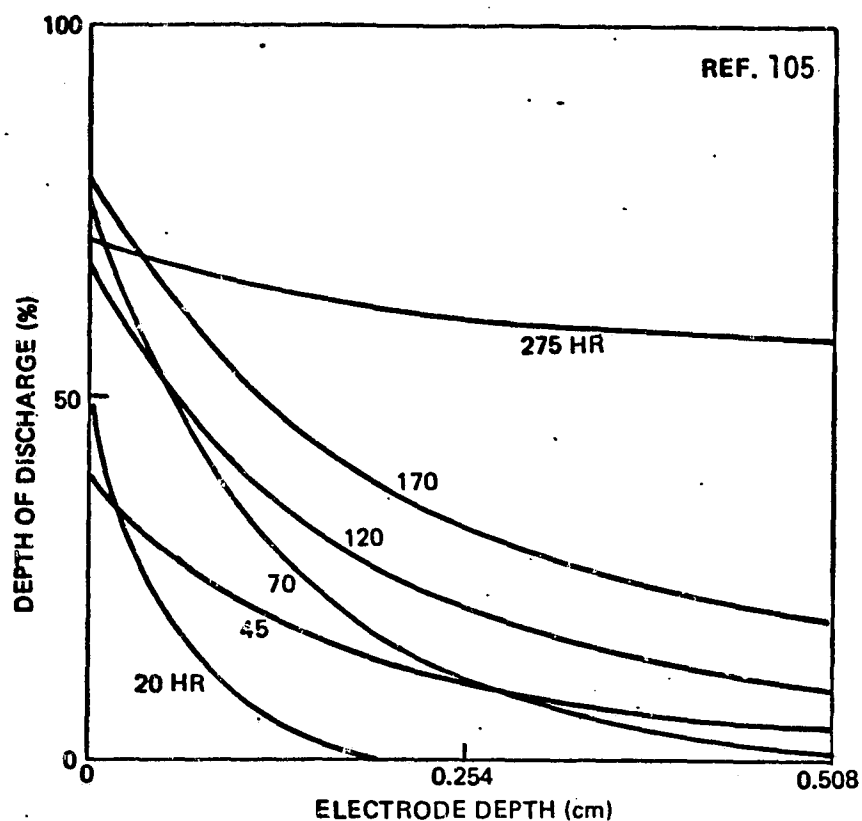


a) DEVELOPMENT OF THE CHOKING PATTERN AT  $2 \text{ mA/cm}^2$

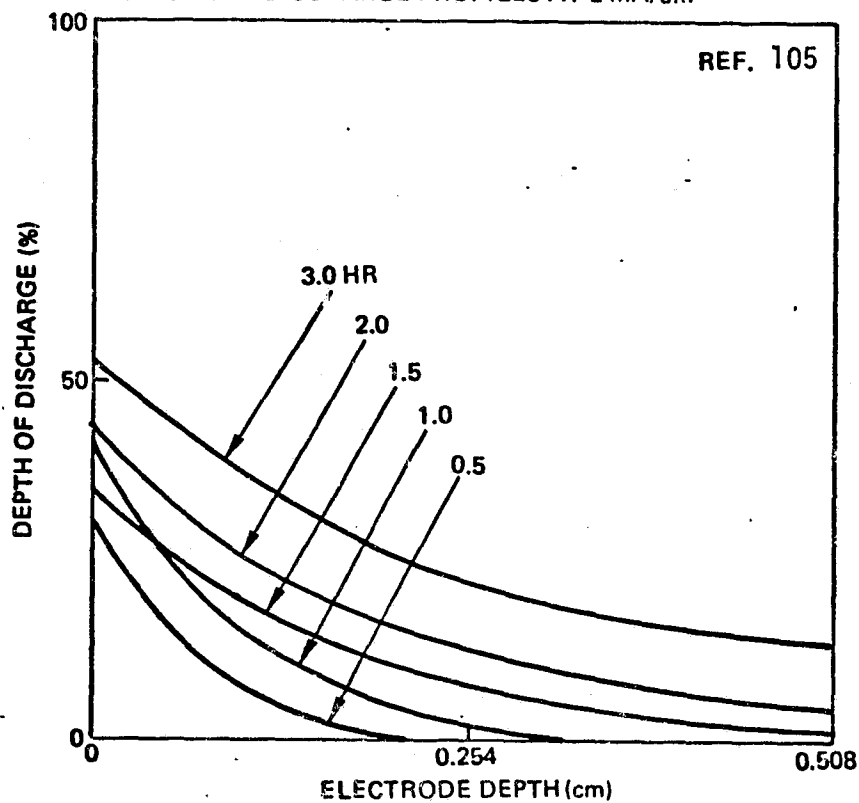


b) DEVELOPMENT OF THE CHOKING PATTERNS AT  $50 \text{ mA/cm}^2$

Figure 7-2. Choking Patterns on Thick Experimental Cadmium Electrodes



a) EVOLUTION OF THE DISCHARGE PROFILES AT  $2 \text{ mA/cm}^2$



b) EVOLUTION OF THE DISCHARGE PROFILES AT  $50 \text{ mA/cm}^2$

Figure 7-3. Discharge Profiles on Thick Experimental Cadmium Electrodes

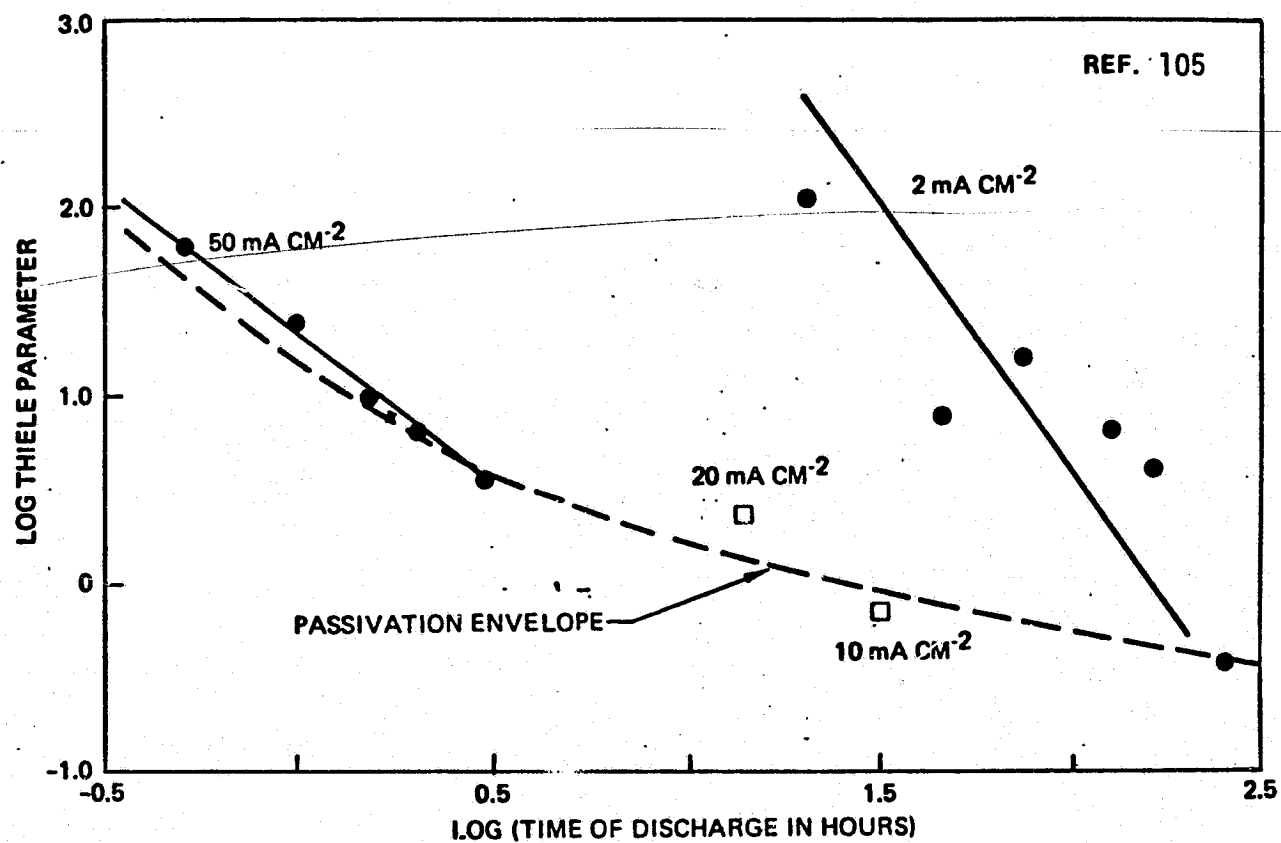


Figure 7-4. Time Evolution of the Thiele Parameter and the Thiele Parameter at the End of Discharge

C-2

- o Large free volume
- o Thin uniform layers of active material (light loading)
- o Thin electrodes
- o Uniform structure with proper pore size

Thus, geometry effects are a major consideration in the design of long life cadmium electrodes.

### Cycling Effects

Recrystallization of active material is one of the important processes in the cadmium negative electrode. The cadmium species are partly soluble, and also the crystal ripening process tends to transform a lot of small, high-surface-area crystals into fewer large ones having much less surface area. This phenomenon occurs in all cadmium electrodes, more intensely in some designs, and less in others. Recrystallization is believed to be more severe with low porosity plates than with high porosity plates, but comparative data are not available on this point. Available data do show, however, that recrystallization is promoted by low charge rates, high operating temperature, repetitive cycling to low depths of discharge, and some conditions of storage, especially open circuit storage in the charged condition. Sometimes overcharge also promotes recrystallization.

In a new cell, large hexagonal platelets of  $\beta\text{-Cd(OH)}_2$  have been observed during the early stage of discharge. These platelets gradually enlarge during the discharge, then during the last part of the discharge there is an accelerated enlargement (Fig. 7-5). The large hexagonal platelets act as substrates for the precipitation of smaller ones, especially during early cycles.

During charge, small platelets convert to cadmium, but many of the large ones do not fully convert (162). The surface of the platelets is smooth, and dissolution takes place mostly at the layer edges. As cycling of a new cell continues, the crystals become larger and more nearly perfect, and a high degree of stacking occurs with the platelets. However, crystal size tends to stabilize with cycling, possibly due to choking.

Nucleation and growth of  $\beta\text{-Cd(OH)}_2$  apparently dominate during the early part of discharge, followed by crystal growth and dissolution of small crystals, with simultaneous growth of larger crystals.

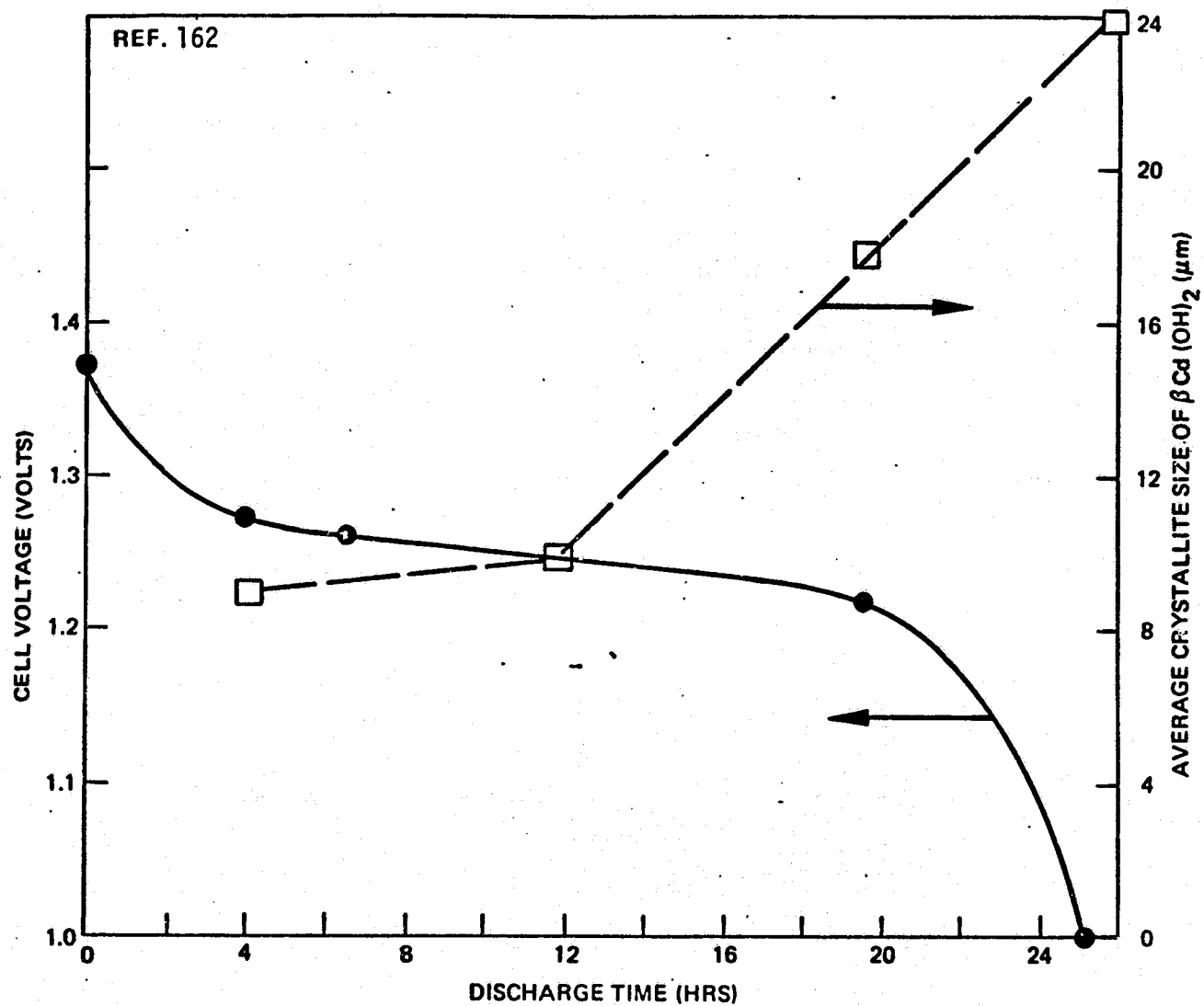


Figure 7-5. Variation of Cell Discharge Voltage and Crystallite Size of  $\beta\text{-Cd}(\text{OH})_2$  During Discharge

Crystal growth has been observed on the external surface of the electrode, with crystals resting on the sinter exterior (162, 61, 99). Of greater importance is what occurs inside the electrode pores. Material migrating from the interior of the electrode toward the outer surfaces can choke up the pores and interfere with mass transport, thus limiting capacity. This choking effect is believed to be a major contributor to the reduction of capacity with cycling (100, 105). Also a factor can be isolation of active material, presumed to occur when the neck of an active pore fully converts to cadmium hydroxide, isolating the inner core of cadmium metal.

Internal strains will make large cadmium hydroxide crystals crack, as observed in scanning electron microscope (SEM) studies (108)\*. Such cracks permit fuller utilization of active material, as shown by deviation from the parabolic law for film growth of cadmium hydroxide (92).

Cadmium electrodes cycled in very dilute (0.1 N) KOH change very little physically (106); only low rates can be supported in such dilute electrolyte, however. The solid state reaction is believed to dominate at this concentration, since the solubility of cadmium species is too low for dissolution-precipitation to be significant.

Very little of the voluminous life data on nickel cadmium cells provides good insight into the cadmium electrode cycle-life behavior. One reason is that good analytical diagnostic methods have become available only relatively recently (163). Another reason is that often the cells fail by drying out, as a result of the positive electrode expanding and wicking up the free electrolyte.

The electrode manufacturing method influences cadmium electrode cycling performance. In one experimental study (50) cycling performance was compared for electrodes made with sintered nickel, sintered cadmium, sintered silver, and Teflon-bonded cadmium hydroxide on silver substrate. Cycle-life behavior at 100 percent depth of discharge in flooded tests is given in Fig. 7-6. The reason for the very poor cycle performance of cadmium impregnated silver sinter is not known. Cadmium sinter electrodes did not have stable capacity because the sinter participated to varying degrees with cycling.

\* Also, private communication, D. Chua

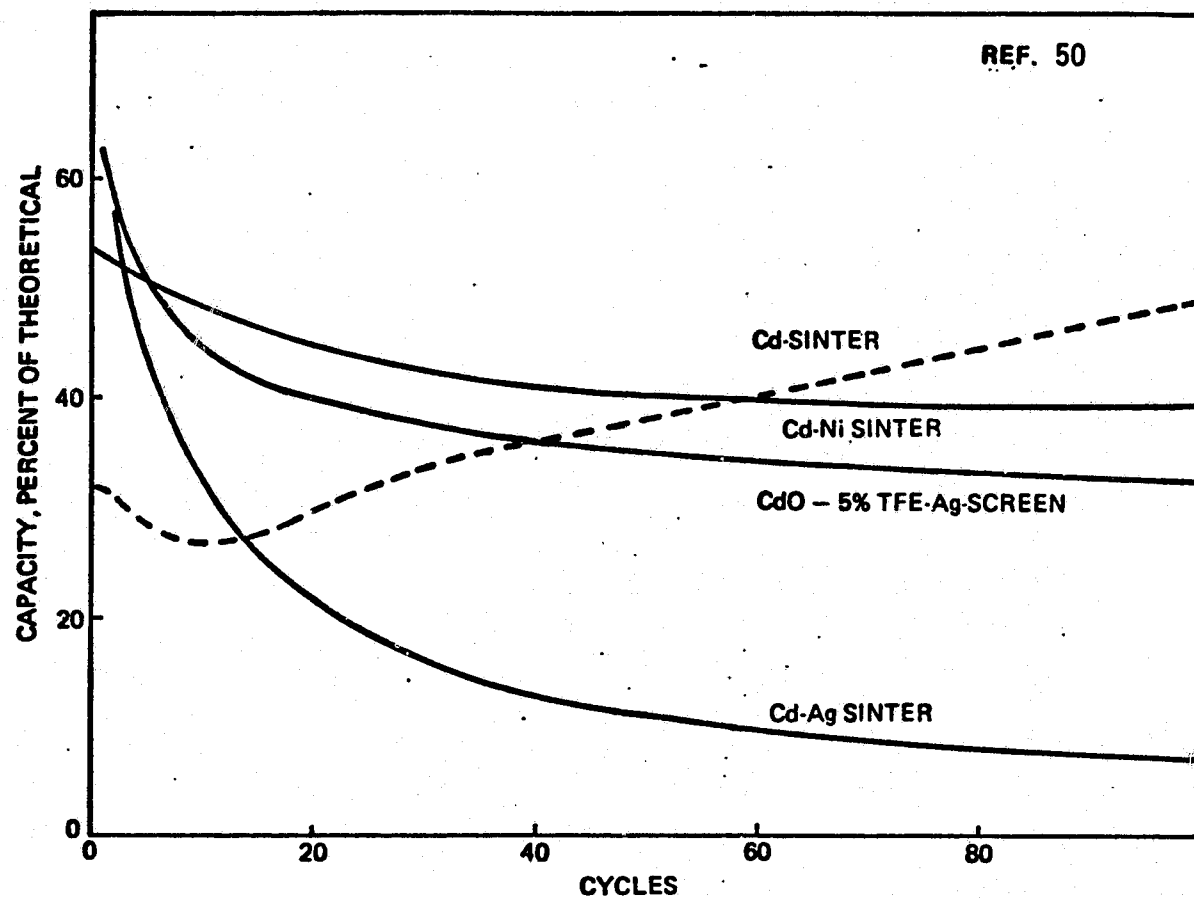


Figure 7-6. Cycle Behavior of Various Negative Electrode Structures

Both the nickel sinter and the Teflon-bonded silver showed stable capacity after the initial break-in cycles. The good performance of the Teflon-bonded electrode suggests that this construction could improve high energy density cadmium electrodes.

Lightly loaded negative electrodes have good oxygen recombination capability, as discussed in Section 6, and fade in capacity at a lower rate when compared with heavily loaded plates. This is illustrated in Fig. 7-7, where capacity fading of a Bell Telephone Laboratories plate loaded to 30 percent of plaque void-volume is compared with fading of a commercial cell-plate loaded to 40 percent. Tests have shown that lightly loaded plates were much more stable (142), although some of the differences may be attributed to other design factors, such as impregnation method, plaque differences, impurity level, and the fact that the tests were conducted in a flooded condition rather than in the semi-starved condition used in sealed cells.

It is clear that lightly loaded negatives fade less than those that are more heavily loaded. Research has not established all the basic reasons why this is so, although attainment of a high void volume is one important contributor (100, 105). The impregnation method could possibly be a factor, and pore size and porosity may also be important. One current research approach starts with a strong, high porosity plaque which is then impregnated to high levels in a manner that preserves high porosity. It will be interesting to see if such plates do fade, and thus help establish whether or not it is loading per se that causes fading.

The cadmium electrode when fully charged is reduced largely to cadmium, and then the metallic cadmium coalesces to a less active state (150).<sup>\*</sup> This condition, called cadmium agglomeration, could be approached in cells that have too high a state-of-charge initially, or which increase their state-of-charge with cycling as the separator oxidizes or as the positive electrode corrodes. Also, in some manufacturing processes the negative electrode is brought to a full state-of-charge during pre-charge setting. No data are available to quantify importance of cadmium agglomeration in cells.

In large nickel cadmium cells uneven current distribution could overstress parts of the electrode and wear them out. Current distribution measurements on nickel cadmium cells suggest that this phenomenon is more important at the nickel electrode than at the cadmium electrode, for the cadmium electrode had the better current distribution (164).

<sup>\*</sup> Also, private communication, P. BRO



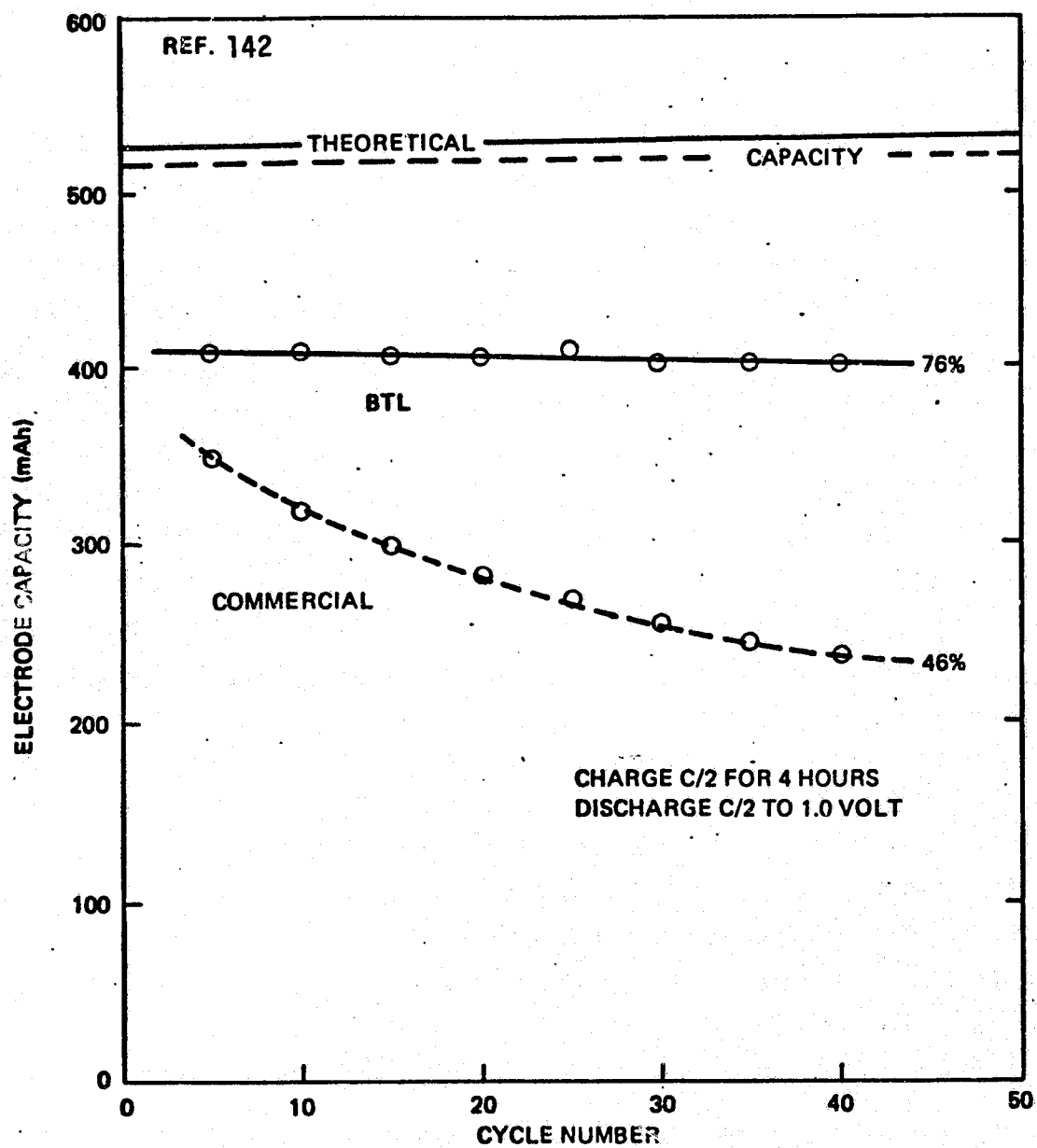


Figure 7-7. Cycle Data—Flooded Negative Electrodes

After long repetitive charge-discharge cycling, the cadmium electrode can develop a second plateau during deep discharge. This non-reversible step, amounting to about 0.15 volts, is attributed to nickel compounds entering into the cadmium during impregnation. The effects of such nickel additions are discussed in Section 9.0.

Cells charged-discharged cycled at high temperature degrade in voltage when returned to room temperature. Both the positive and negative electrodes lose voltage, as shown in Fig. 7-8. The direction of the voltage change at the cadmium electrode favors hydrogen generation, which is common after a large temperature excursion (132). The cause of the voltage change, not fully understood, is believed to be a phenomenon other than the increased resistance such as encountered when a cell is from 25°C to -40°C (58).

Cadmium in nickel cadmium cells sometimes migrates into the separator and positive plates. The cause of this migration is not well understood. Possibly the  $\text{Cd}(\text{OH})_2$  particles acquire a negative charge by absorbing  $\text{OH}^-$  ions, then migrate electrophoretically toward the positive electrode during charge. Measured mobilities of such particles have been high enough to account for the observed migration (166). An important finding was that  $\text{Cd}(\text{OH})_2$  mobility in KOH increases substantially with increasing amount of carbonate. For example, raising the concentration of  $\text{K}_2\text{CO}_3$  from 0.8 to 9.0% in 34% KOH increases the mobility from  $0.8 \times 10^{-4}$  to  $1.8 \times 10^{-4}$  cm/sec per V/cm. Mechanisms for reducing  $\text{Cd}(\text{OH})_2$  to Cd metal in the separator have not been established.

#### Synchronous Orbit Operation

One of the most comprehensive series of tests defining the changing behavior of the cadmium electrode during cycling was the work done by COMSAT Laboratories on TELESAT cells (167, 168, 169). These investigations followed those done on INTELSAT cells (170). The INTELSAT cells differed from the TELESAT cells in that they did not have silver catalyst in the negative electrodes, nor were they made with cadmium in the positives. The greater amount of cadmium migration and voltage degradation observed on the TELESAT cells may be attributable to the silver or possibly other factors.

The TELESAT test conditions simulated the actual operation of an earth-synchronous spacecraft having two eclipse seasons per year. Between eclipse seasons the cells

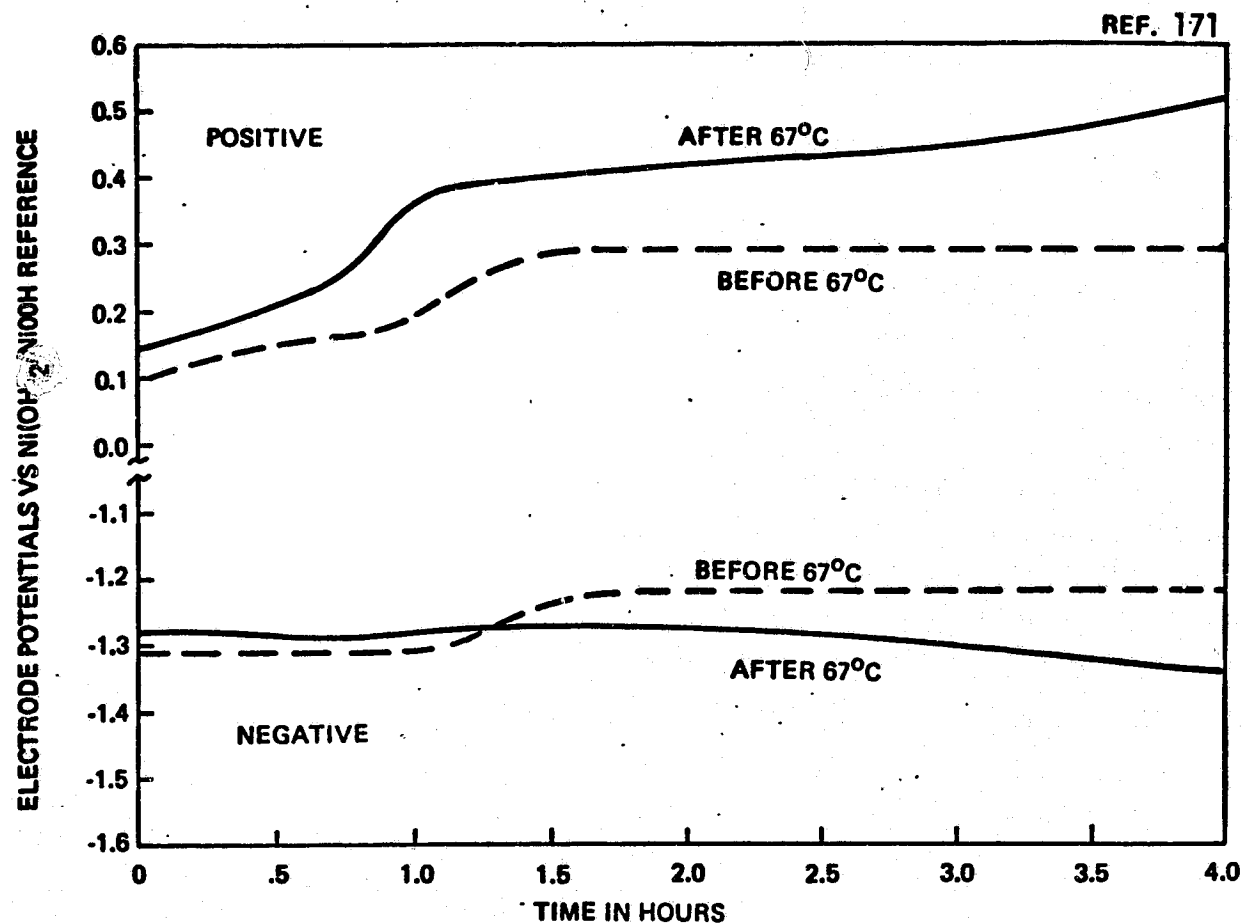


Figure 7-8. Typical Charge Curves for Positive and Negative Electrodes at 25°C Before and After Long Term Cycling at 67°C

were on open circuit, but recharged monthly. The terminals were always up, which may have been important because thickening at the lower portions of the cadmium electrodes was observed, similar to the thickening of the INTELSAT cells (172, 170, 61) cited in the section on charging effects.

The TELESAT tests (Table 7-1) showed that about 10 percent of the cadmium had migrated from the cadmium electrode into the separator and positive electrode. Also, the percentage increased more with time than can be accounted for by separator oxidation. Not shown in this data is the fact that after cycling, many of the cells were negative limiting on discharge.

An unusual finding in these tests was that the cadmium electrode efficiency increased with use (Table 7-1). No experiments were conducted to try to understand this effect, however. If it had not been for this efficiency improvement with time, performance of the cells would have been much worse. It would be interesting to learn why the efficiency increased, and under what operational conditions such an increase may or may not be expected. One possible explanation was that pore volume increased due to conversion of  $\text{Cd}(\text{OH})_2$  to  $\text{Cd}$ , since  $\text{Cd}(\text{OH})_2$  is the ultimate source of oxygen for nickel electrode corrosion and separator oxidation.

TABLE 7-1: ANALYSIS OF CADMIUM ELECTRODE IN SIMULATED SYNCHRONOUS ORBIT TESTS

		LOT 2			LOT 4		
		Nearly New Cell	Nearly New Cell with Acceptance Testing	28 Months Simulated Orbit Testing	Nearly New Cell	18 Months Simulated Orbit Testing	28 Months Simulated Orbit Testing
		024-L02	026-L02	034-L02	080-L04	084-L04	085-L04
Capacity	Total Cadmium Capacity (Ahr)	20.14	19.84	18.14	19.64	18.60	17.93
	Flooded Negative Capacity (Ahr)	14.51	13.61	14.50	14.07	14.11	14.36
	Negative Capacity Utilization-%	72.0	68.6	79.9	72.0	77.2	80.1
Breakdown	Positive Capacity (Ahr)	8.87	8.93	8.68	9.15	9.05	9.05
	Residual Charged Cadmium (Ahr)	0.30	0.20	2.90	0.34	1.53	2.88
	Usable Precharge (Ahr)	2.27	2.39	2.74a	1.00	1.94	1.42
	Unavailable Precharge	0.30	0.20	2.90b	0.34	1.53	2.88
	Total Precharge (Ahr)	2.57	2.59	5.64	1.34	3.47	4.30
	Overcharge Protection (Ahr)	3.37	2.29	3.08	3.92	3.12	3.89
	Residual Discharged Cadmium(Ahr)	5.33	6.03	0.74	5.13	2.96	0.69
Cadmium Distribution	Cd in Negative Plates (gm)	42.20	41.59	38.03	40.96	38.99	37.58
	Cd in Positive Plates (gm)	1.48	1.80	3.00	1.07	2.28	3.10
	Cd in Separator (gm)	0.21	0.27	1.42	0.23	0.50	1.37
	Total Cd in Cell (gm)	43.89	43.66	42.45	42.26	41.77	42.05

a = Flooded Plate Measurement

b = Analysis After Flooded Plate Measurement

REF. 166

## Failure Mechanisms

Some nickel-cadmium cell failures are directly or indirectly attributable to phenomena occurring at the cadmium electrode. These failures generally fall into three categories: internal shorting, loss of capacity and electrolyte entrapment within the nickel and cadmium electrodes resulting in a drying out of the separator. While these failures are generally accepted, the mechanisms by which they occur are both complex and controversial.

Table 7-2 lists some of the mechanisms reported as important contributors to cadmium electrode deterioration. Previous sections have treated these chemical, electrochemical and physical processes in some detail. All of these mechanisms have been demonstrated experimentally in tests of complete cells, single electrodes, or simulations. However, only relatively recently has an attempt been made to relate these mechanisms to operating, design, and manufacturing variables. While low earth orbit, synchronous orbit, and deep space probes impose wide variations in battery operating requirements, there is little indication in the literature that specific design and/or manufacturing techniques have been developed to meet these requirements. A notable exception is recent work sponsored by USAF which has addressed failure mechanisms in terms of analytical techniques and the contribution of certain design and fabrication variables to cell failure (15).

Most of the literature relating to failure analysis has been devoted to cell failure in charge-discharge cycling. Thus, most of the failure mechanisms are discussed in this section. Moreover, many of the failure modes are operating simultaneously. Halpert (173), in a study of failure mechanisms, found considerable variation from cell to cell and from electrode to electrode in a single cell so that isolating a single chemical or physical cause for failure was not possible. He found evidence of both cadmium and electrolyte migration as well as carbonate contamination. Cadmium electrodes were found to absorb about twice as much electrolyte as the nickel oxyhydroxide electrodes. Ford (174) in a NASA/Goddard study of spare OAO cells, noted abnormal overcharge characteristics which were attributed to excessive cadmium pre-charge during manufacturing combined with negative "capacity fading" during cycling. The most recent NASA/Goddard Battery Workshop (175) emphasized the need for better manufacturing controls to assure electrode and cell reproducibility. In this way, failure mechanisms can be identified with more certainty and related to electrode design and operating parameters (e.g. plaque characteristics, loading method and level, contamination, DOD, charge rate, discharge rate).

TABLE 7-2

CADMIUM ELECTRODE FAILURE AND DEGRADATION MECHANISMS

1. Decrease in discharge efficiency
2. Decrease in discharge voltage (decrease in negative voltage)
3. Second plateau on discharge
4. Cadmium Isolation
5. Pore Choking
6. Cadmium hydroxide crystal growth
7. Formation of Less active form of cadmium hydroxide
8. Migration within cadmium electrode
9. Cadmium migration to separator and positive electrode
10. Improper setting of precharge
11. Increase in Cadmium pre-charge
12. Contamination by carbonate, calcium and magnesium
13. Electrolyte migration
14. Flooding of pores
15. Poor oxygen recombination
16. Hydrogen generation
17. Shorting
18. Broken tabs and header weldments

## 8.0 CHARGING EFFECTS

### General Effects

To best understand the effects on the cadmium electrode of different charge methods and conditions, it is helpful to review the applicable electrochemical principles.

Microcrystalline deposition during charging depends on the formation of new growth centers or nuclei, a process favored by high current density and low temperature, both of which are associated with high overpotentials. High current density means more ions per unit area, but raising the current density and overpotential will not increase the number of nuclei indefinitely (128). Low temperature does slow down crystalline growth rate, but apparently more significant is the accompanying reduction in crystal growth rate. Foreign substances almost always reduce grain size by providing sites for the formation of new nuclei. Thus, high charge and discharge rates and low temperature promote the formation of small crystals (98, 58, 107).

During charge at a rate of greater than about  $C/4$ , small cadmium crystals are formed, and the cadmium utilization is good during the subsystem discharge. For example, Fig. 8-1 from Ref. 98 shows that, at high charge rates, cadmium utilization is greatest, especially in the interior of the electrode. This phenomenon was more pronounced after repeated charge-discharge cycling. The residual cadmium content was uniformly distributed in the electrode, except at the surface where it was always substantially less. In another experiment the discharge did not affect performance when the cell was charged at its  $C$  rate (99). With high-rate charging, choking may be less important than coverage of cadmium metal by the discharged cadmium hydroxide.

Fig. 8-2 shows smaller crystals are formed at high charge rates although there is a leveling off at rates above  $C/2$  (98). The crystals are smaller at the surface than in the interior, but as charge-discharge cycles are accumulated the crystal size increases more rapidly at the surface than in the interior.



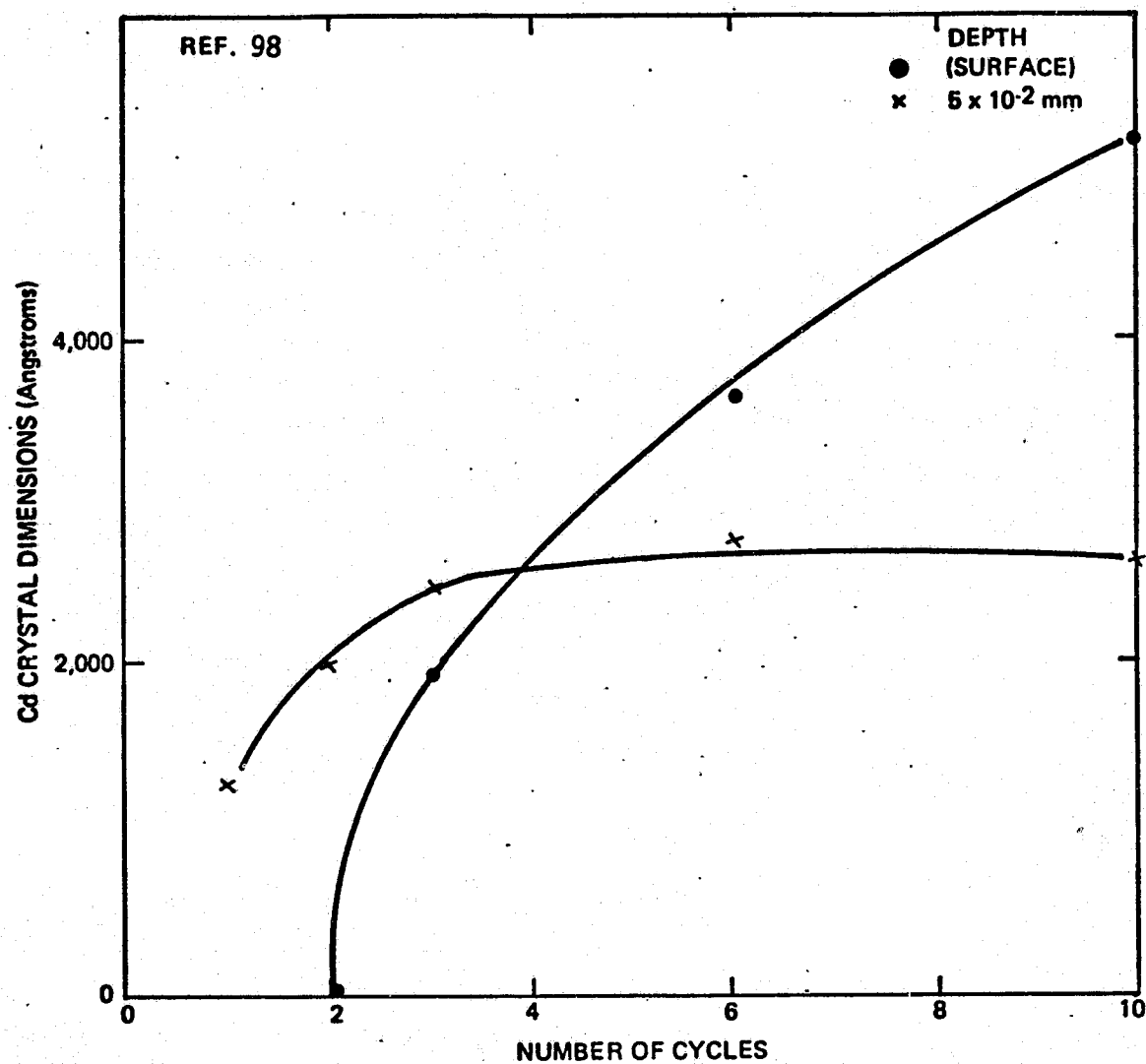


Figure 8-1. Dimensions of the Residual Cadmium versus Number of Cycles

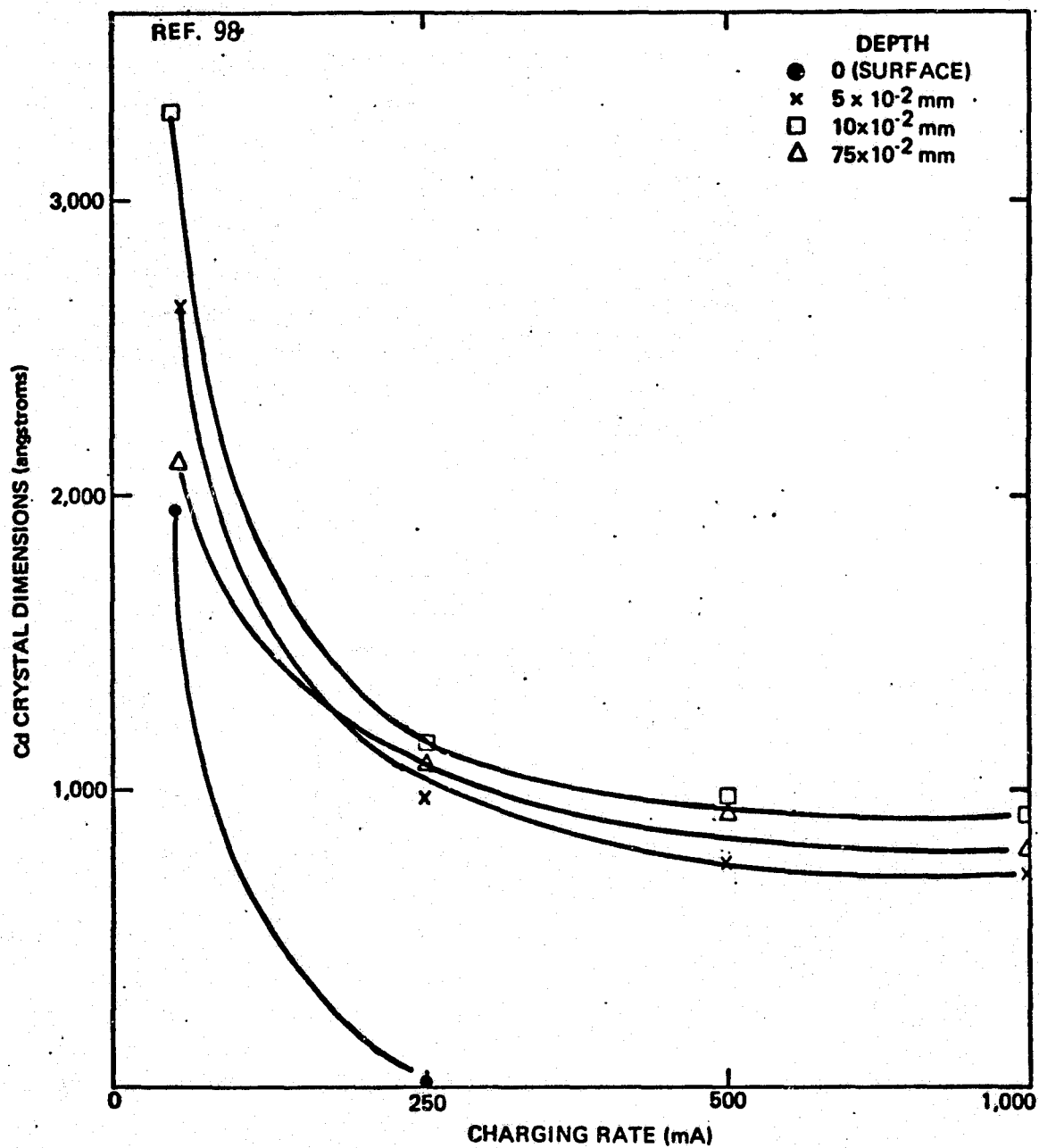


Figure 8-2. Dimensions of Residual Cadmium Crystals versus Charging Current

The contribution of high-rate charge to better, finer crystal structure on cadmium electrodes has long been known, but only recently has high-charge rate been related to longer cycle life (113). The useful life of 1.2 Ah cells charged at a 2-C rate was found to be about twice that of cells charged at a 0.1-C rate. Not known, however, was the contribution of the negative electrode, although one would expect it to be a factor.

The surface area of a cadmium electrode was measured periodically during a nine-month continuous overcharge (176). The overcharge continuously reduced the cadmium surface area (Fig. 8-3) and discharge of the cell did not increase its surface area.

In another test (176), cells cycled for three months lost much of their cadmium surface area (Fig. 8-4). One electrode was then charged, and it showed more surface area. Another electrode was removed from the cell and fully discharged. It showed no significant surface area recovery until it was cycled a few times, and then discharged. Then the improvement in surface area was substantial.

These tests showed that both overcharge and cycling cause recrystallization which reduces electrode surface area. Discharge of a cell doesn't help much, because much of the excess cadmium is not forced to discharge. Capacity cycling outside the cell forces this material to discharge, and one or more subsequent charges will help re-establish a fine crystal structure.

Overcharge reduces cadmium surface area, but it also breaks down large cadmium hydroxide crystals, making this hydroxide available. This was illustrated by a test (Fig. 8-5), in which an electrode was cycled then overcharged for 64 hours, and returned to the cycling regime (99). After the extended overcharge the electrode capacity increased, as shown by the higher electrode efficiency, but the improvement lasted for only ten cycles. The pH gradient cited by Will (106, 91) is probably important in dissolving cadmium hydroxide crystals during overcharge.

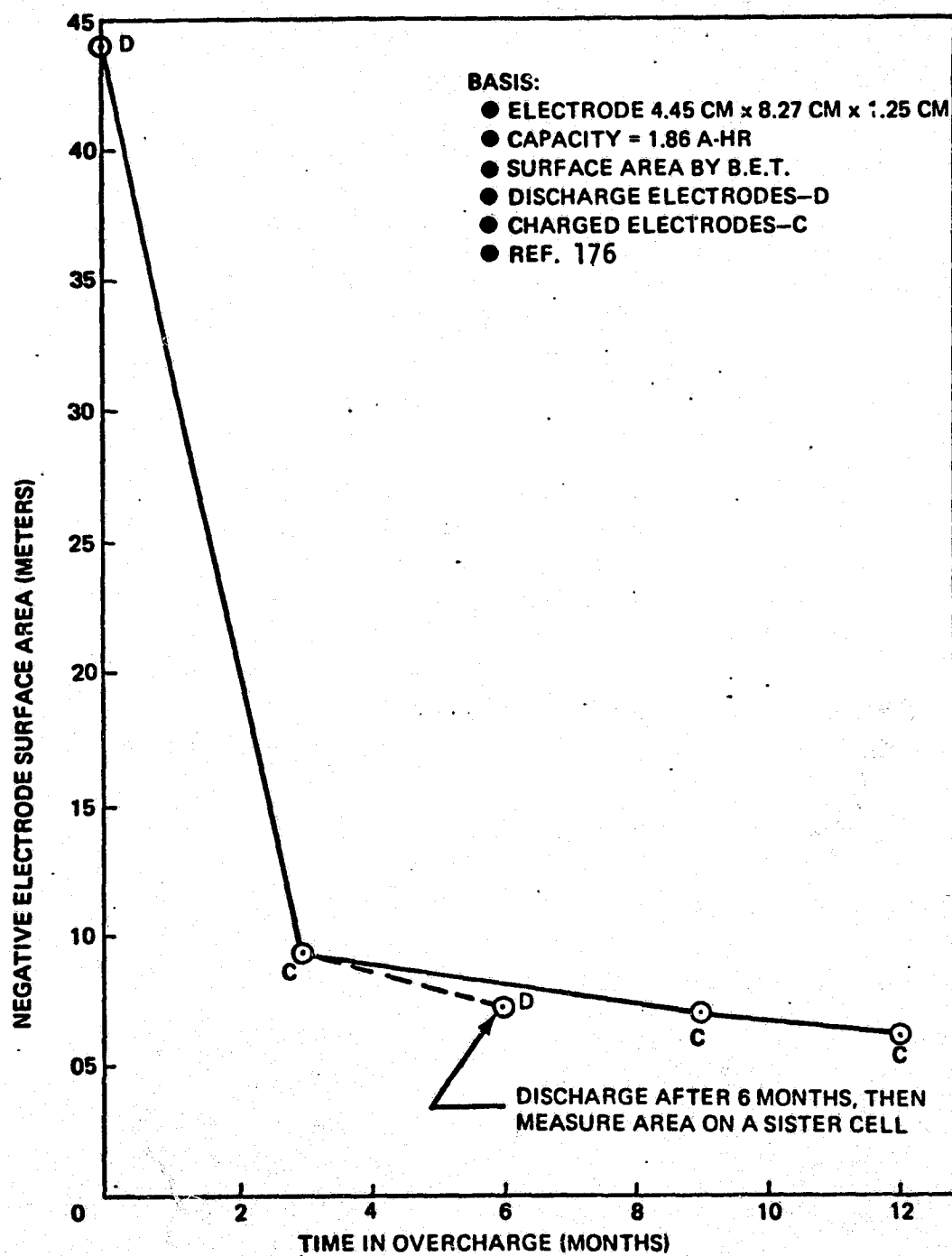


Figure 8-3. Effect of Continuous Overcharge on Cadmium Electrode Surface Area

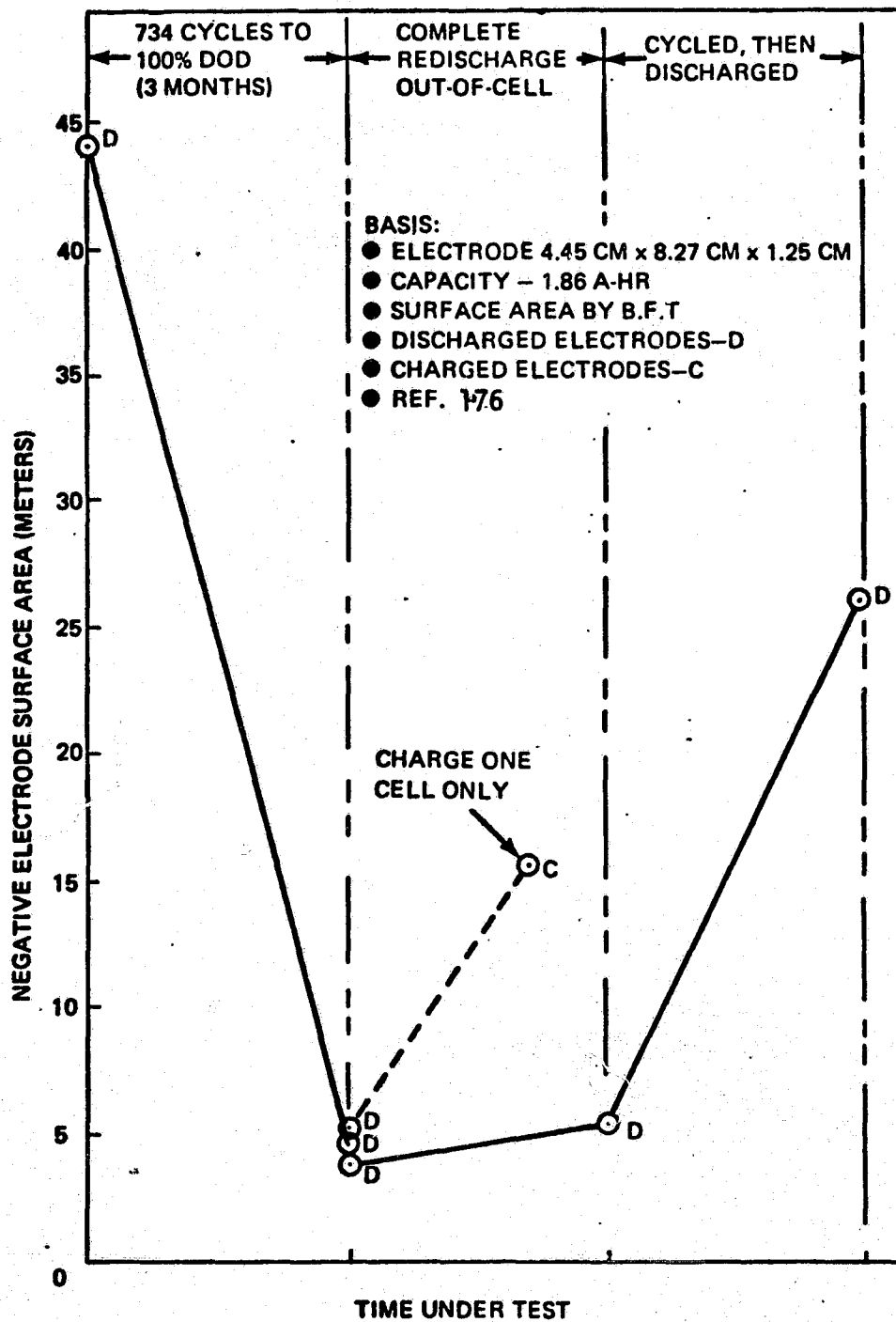


Figure 8-4. Effect of Cycling on Cadmium Electrode Surface Area

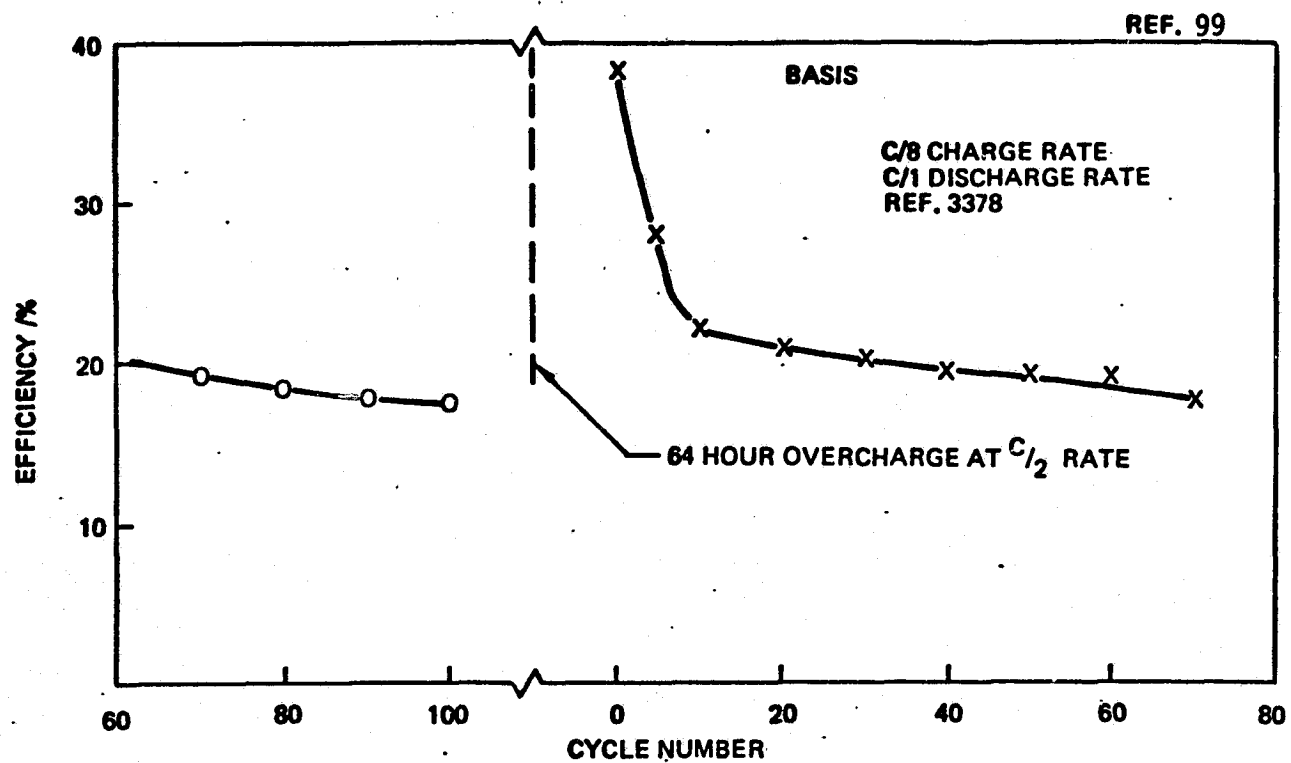


Figure 8-5. Effect of Overcharge on a Previously Cycled Cadmium Electrode

## Pulse Charging

Charging with current pulses and asymmetrical ac charging methods have improved capacity and high-rate capability of a variety of battery systems, including nickel cadmium. In one nickel cadmium study, four charging modes were compared:

- o Constant current dc at 10A (2C)
- o Positive pulse, charge 50A for 2 ms, open circuit 14 ms
- o Romanov type reflex, charge 50A for 3 ms, discharge 3A for 8 ms, open circuit 5 ms
- o McCulloch type reflex, charge 15A for 12 ms, discharge 50A for 0.2 ms, open circuit 4 ms

The average charge rate was the same for each method --- 2C (10 amperes). At 25°C this rate gave about the highest capacity for the flooded, vented nickel cadmium cells tested (177, 178). A C/2 rate made only a small improvement.

Fig. 8-6 shows how each charge method affected the capacity of the cadmium electrode for a variety of average charge rates. The most improvement came with pulse methods that provided some negative pulse energy, that is, a little of discharge with each pulse (reflex charging). Further tests on vented batteries using a 2C rate at -20°F, established the importance of the negative pulse (Fig. 8-7). The tests showed that for the conditions investigated, maximum capacity is attained when the negative pulse is at least 2.5 milliwatt-seconds. The wave form appears to be unimportant, whereas the amount of discharge and the frequency do appear to be important.

An important finding from these tests was that the lost capacity of both vented and sealed cells could be restored by one positive-pulse charge-cycle. The discharge curves of a vented cell before and after pulse charging show that the capacity was restored to its full initial value (Fig. 8-8). Scanning electron micrographs of the cadmium electrode showed that cadmium hydroxide crystals in a fresh, discharged condition were about one micrometer in size, increasing to over 50 micrometers when tested in a regime producing fadeout, and then reducing to about 3 to 4 micrometers after one pulse cycle (178). This demonstrated that pulse charging can convert a degraded cadmium electrode structure to a much more favorable morphology.

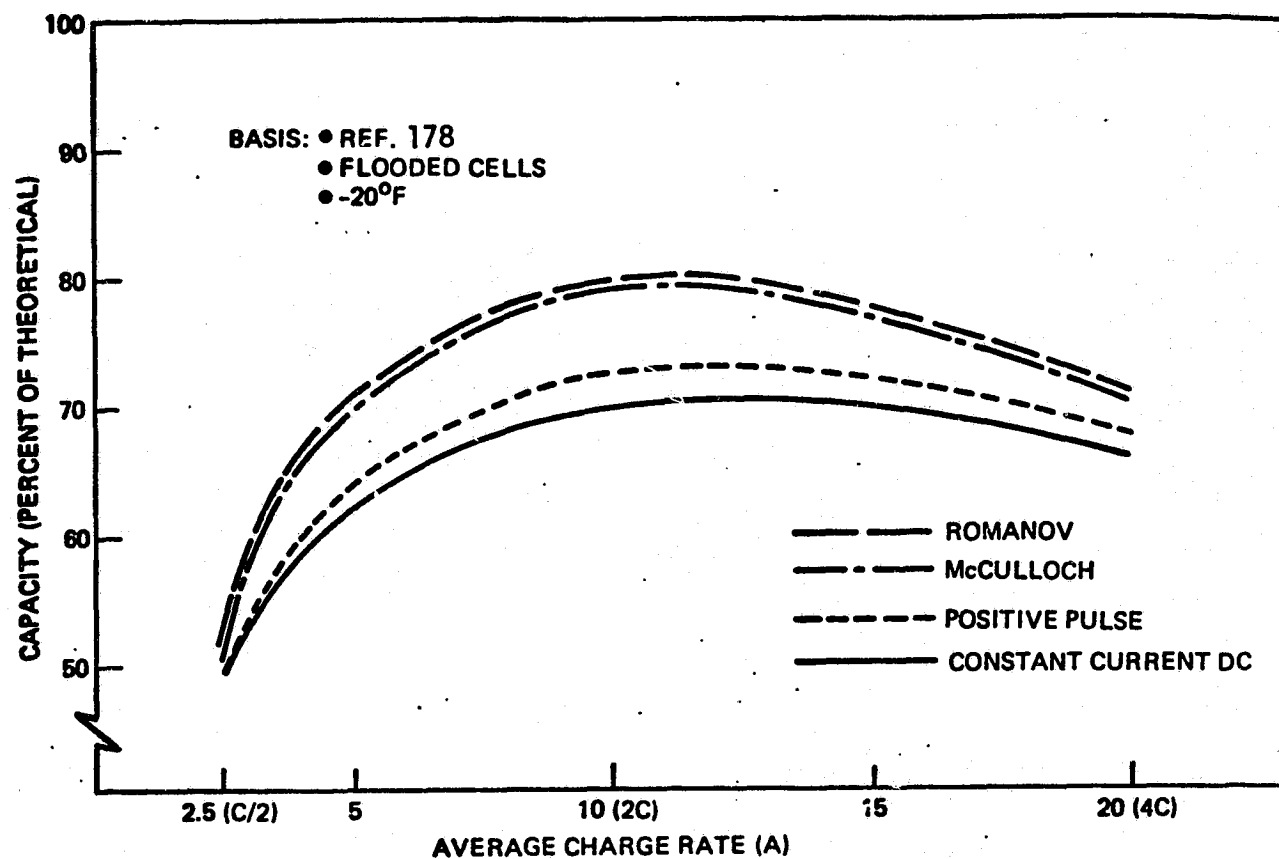


Figure 8-6. Capacity of Cd Electrodes With Pulse Charging



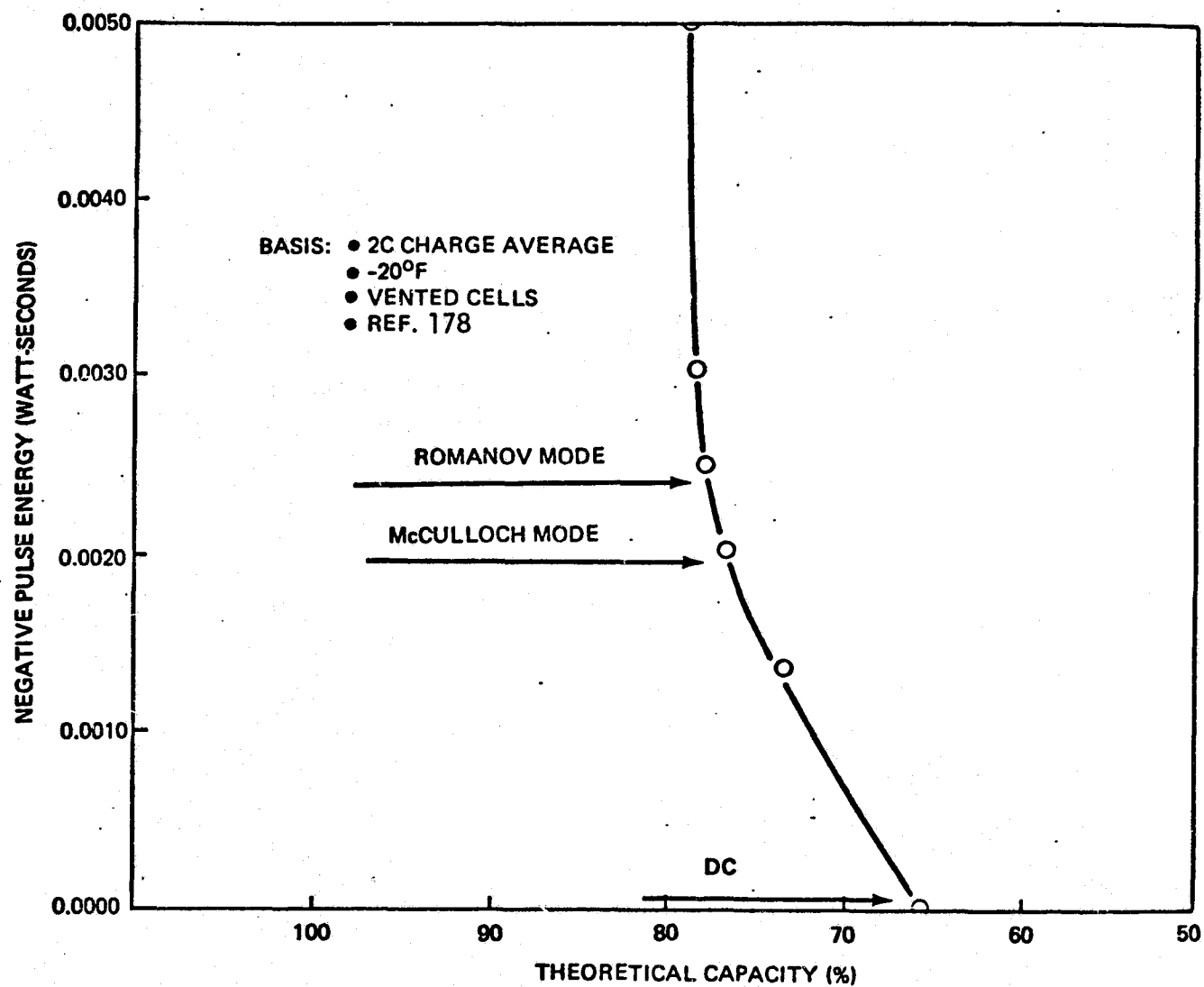


Figure 8-7. Capacity of Cd Electrodes as a Function of Negative Pulse Energy

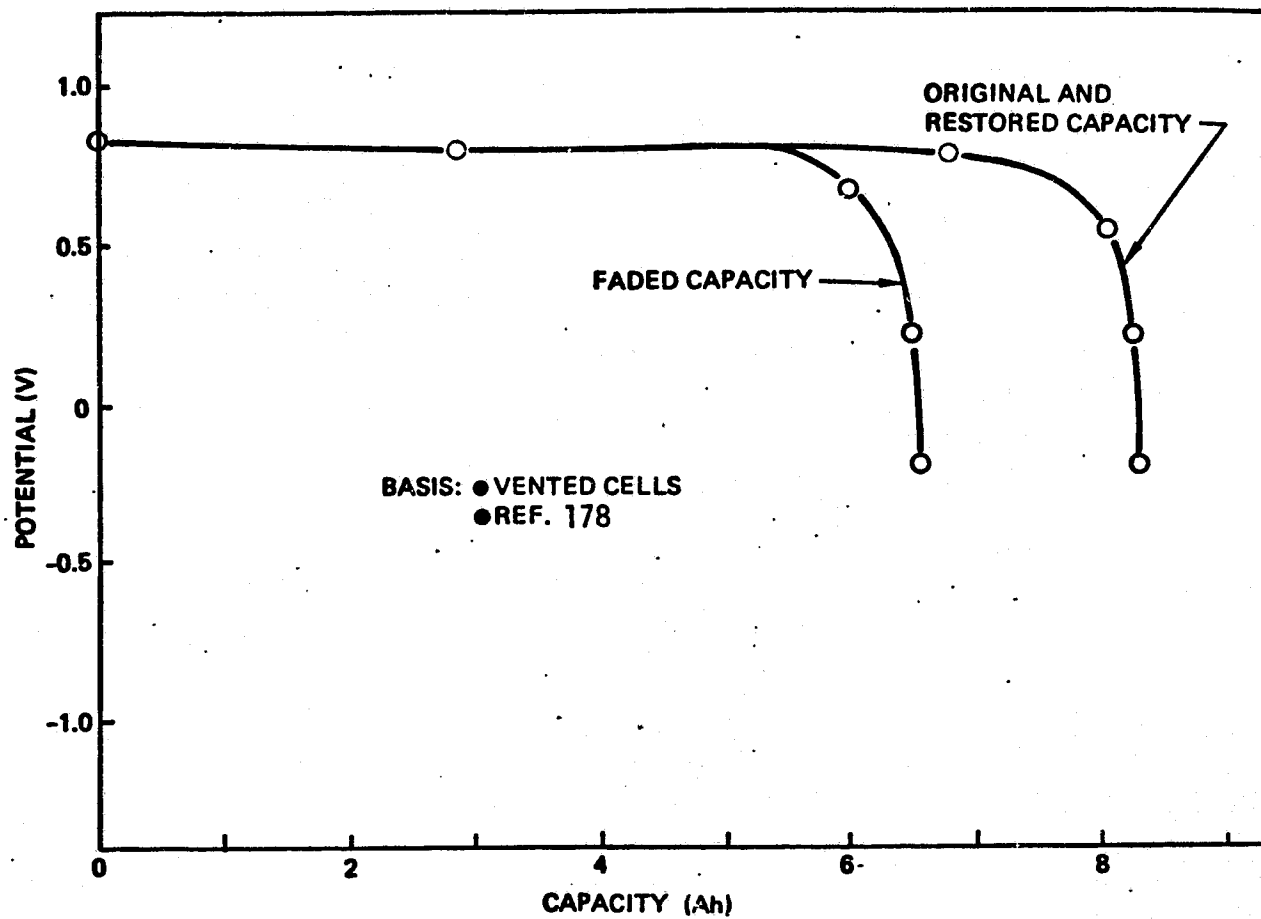


Figure 8-8. Cadmium Electrode Capacity Lost by Fadeout and Restored by Pulse Charging

Why pulse charging results in improved electrodes is not fully understood. The large instantaneous currents could be a factor, but they are not the full explanation because the improved performance is frequency dependent\*. Current pulses, because of their penetrating power give uniform coverage in electroplating. The small discharge associated with each charge pulse could conceivably give a type of electrolytic polishing, similar to that obtained commercially with alternating current. Conceivably, the pulses could also break down the double layer. These are only hypotheses, provided in the absence of recognized explanations of this phenomenon.

An important consideration with sealed cells is avoidance of hydrogen gassing, which could occur during the high voltage pulses. Also, the high internal resistance of large electrodes makes pulse charging of large cells difficult. Nonetheless, the potential gains of pulse charging warrants its consideration for some sealed cell applications.

#### Charged Storage

One important battery charge-control question for earth-synchronous orbit applications is how to best treat the batteries during the rest period between eclipse seasons. In one series of real-time tests, with Intelsat IV 18 Ah cells, two storage modes were compared; (1) Charged and open circuited, but recharged every 30 days at C/18 for 24 hours, and (2) continuous trickle charge at C/36 (172, 170, 61). Cells were periodically removed from the test and analyzed. The trickle charge was best in all respects. Other observations from this test were:

1. The increase in carbonate in the cells was the same for both storage methods, being 0.82 grams  $K_2CO_3$  per cell per year. Less carbonate was produced during storage than the 6.0 grams per cell that was in the plates initially.
2. Discharge voltages in the cells during the eclipse season were higher and more closely grouped when the cells were being trickle charged.

\* Private communications, O. C. Wagner

3. The trickle charged cells retained their capacity whereas the open-circuited cells degraded to the point where some cells were negative limiting.
4. On disassembly, the separators of the open-circuited cells were sticking to the cadmium electrodes, whereas there was practically no sticking in the trickle-charged cells. The surfaces of the open circuited cells were not uniform.
5. Thickness of the trickle-charged plates was uniform within  $\pm 2\%$ , whereas the plates of the cells on open circuit has large variations in thickness, with up to 25 percent growth at the bottom regions after eight eclipse seasons. This increase came not from swelling of the plaque, but from migration of cadmium to the plate surface.
6. Distribution of cadmium was uniform ( $\pm 3$  percent after nine eclipse seasons) on the discharged plates of the trickle charged cells, but varies widely ( $\pm 23\%$  to  $-31\%$ ) in the plates of the open circuited cells.
7. Cadmium in the open-circuited cells had migrated to the outer surface, blocking pores near the surface, and generating large cadmium hydroxide crystals (up to 50 micrometers) on the surface. By contrast, the trickle-charged cells did not have enough cadmium migration or blockage to be noticed, and cadmium hydroxide crystals were only about one micrometer in diameter.

These tests showed that at least in synchronous-orbit applications, open-circuit between eclipse seasons is more harmful than trickle charge. Migration and recrystallization of cadmium are the important degradation mechanisms.

## 9.0 ADDITIVES AND IMPURITIES EFFECTS

Many researchers have tried to improve the performance of the cadmium electrode by introducing foreign substances into the cell. However, the scope of their experiments and documentation of their results often was not complete enough for rigorous evaluation of the diverse effects of such additions. The added impurities may be gases, liquids or solids, and the method of their incorporation can significantly affect the results.

### Inert Gases

Gases introduced into the cell are usually nitrogen from the air or chemically inert helium which is sometimes injected into the cells to aid in detection of leaks. These contaminating gases can accumulate in the negative plate pores and conceivably impede the diffusion of oxygen which must be transported into the negative plates for recombination. In practice, however, these contaminating gases appear to have little or no effect on reaction rates. For example, nitrogen gas introduced into a cell at various pressures did not change the gas recombination rate (127). In some applications inert gases such as helium and nitrogen might be beneficial because they reduce the stress on the plates during gassing (179, 180). In nickel cadmium cells, this would generally be important for the nickel positive electrode, although the cadmium negative electrode could also be stressed during reversal.

Air entrapment in the negative electrode can keep electrolyte from filling the fine pores initially but after cycling some of these pores wet out, altering the electrolyte distribution (181, 182). In the smallest pores surface tension forces are more important in limiting wetting than is air entrapment. Here the Cassie-Baxter effect predominates, the contact angle on microporous structure being much increased, producing a wet-proofing effect.

### Beneficial Additions

Some additives are beneficial, although they may also have undesirable effects. In general the beneficial additives are those that reduce the size of crystals formed on the cadmium electrode providing large area for the reaction. A useful additive must not increase polarization or retard the reactions in any way. however.

Indium has been a successful expander in cadmium electrodes. It can be added during processing either as indium nitrate (1) or indium hydroxide (32). It improves high-rate performance at low temperature, and also somewhat at room temperature. The effectiveness of indium as an expander comes in part from its low solubility in KOH and its similarity to cadmium in axial ratio, ionic radius, and electrode potential (32). Other research shows that indium can be incorporated in the crystal lattice of cadmium oxide (119). Sweeping potential studies show that indium additions suppress the initial current peak associated with passivation, but introduce additional peaks at greater anodic potentials, thus delaying passivation (82). Some indium probably becomes incorporated into the cadmium hydroxide crystal lattice, changing the type and increasing the number of imperfections.

Indium addition has also improved the energy density in nickel cadmium cells. By improving the efficiency of the negative electrode during cycling, it has been possible to use relatively thick electrodes\*. On the other hand, one investigator said that he found no benefit from adding indium\*\*.

Very little quantitative information is available on the effects of indium. From one study, a watt-hour efficiency increase of 20 percent at  $-20^{\circ}\text{C}$  (129, 183, 184) was reported. In a recent test one percent indium was added to mold-pressed cadmium electrodes and cells made from these electrodes were subjected to low-current cycling at  $125^{\circ}\text{F}$  to induce fadeout. Performance before and after the fadeout regime was unchanged for cells with indium (Figure 9-1) whereas control cells showed large reductions in discharge voltage and capacity (185). Photomicrographs showed large cadmium hydroxide crystals on electrodes without indium, whereas electrodes with indium had a spongy surface composed of small particles.

Acetate salts, when impregnated into both positive and negative plates, are claimed to improve charge retention (140). This may result from lowered nitrate impurity levels, or from different morphology because cadmium is precipitated as a metal in this process. It should be noted that cadmium electrodes impregnated in either cadmium chloride or cadmium acetate have lower utilization and higher charging voltage than plates made from cadmium nitrate (112).

\*Private Communication, A. Fleischer.

\*\* Private Communication, K. Beccu.

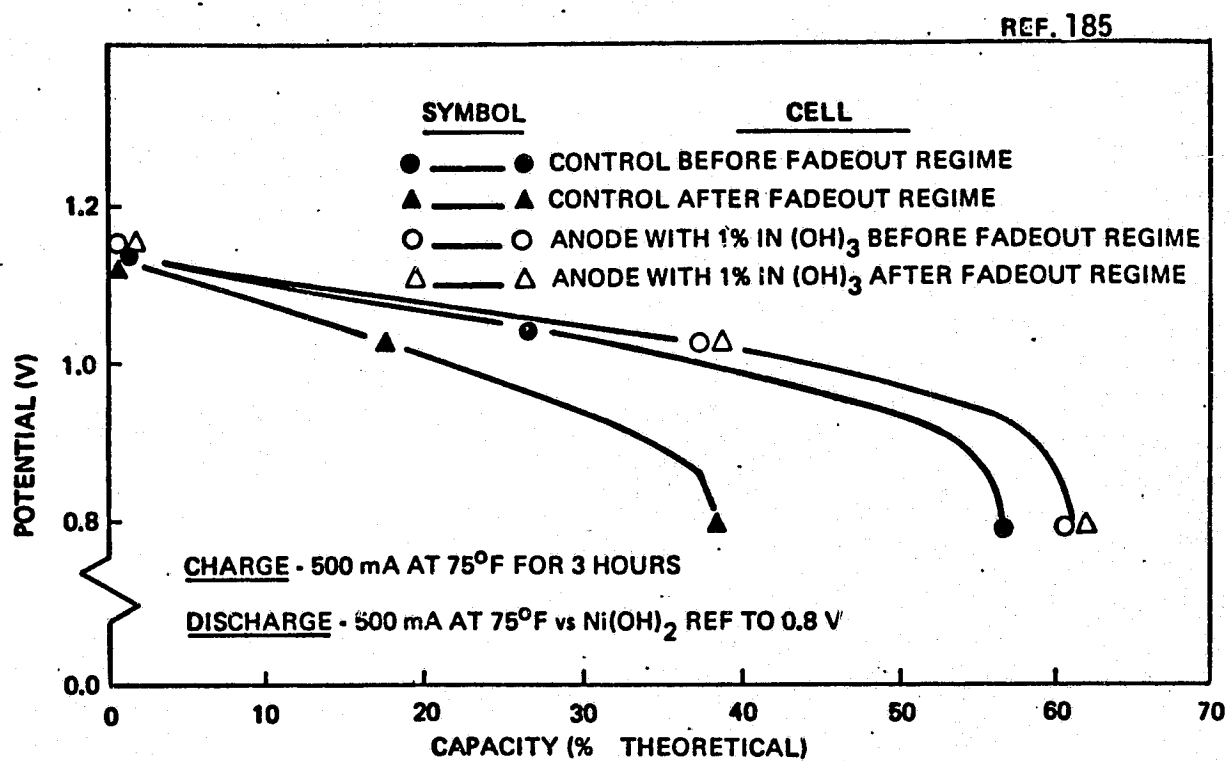


Figure 9.1. Effect of Indium Additions on Mold-Pressed Cadmium Electrodes

A similar phenomenon occurs with cadmium electrodes made from cadmium iodide, which forms a type of cadmium hydroxide that has high resistivity as a result of fewer bridged  $\text{OH}^-$  groups (34).

Alkali-soluble cellulose compounds were found to prevent fadeout of the cadmium negative electrode (112, 186). In vented cells, these soluble compounds are produced by the cellulosic separator. Saturation of KOH electrolyte in cadmium-air cells with zincate ions or aluminate ions was reported to improve the efficiency of the cadmium electrode (187). However, no supporting data were provided.

Silver is a useful additive to the negative electrode, enhancing oxygen recombination. Many of today's aerospace cells contain silver dispersed in the anode for that purpose (35). The silver, being in direct contact with the negative material remains in the fully reduced, metallic form and doesn't form partly-soluble silver oxide which could move within the cell. Even though silver does not migrate when used this way, it causes side effects. In one series of simulated synchronous-orbit tests, TELESAT cells with silver showed more cadmium migration and voltage degradation than did INTELSAT cells that had no silver (167, 166, 34). However, the observed phenomena might have been caused by other differences among the cell groups such as cadmium added to the positive plates of the TELESAT cells, and different amounts of carbonate. The oxygen catalysis effects of silver are discussed in the section on oxygen recombination.

Cobaltous ions increased the capacity of cadmium electrodes (34). The  $\text{Co}^{++}$  ions form on the surface of cadmium hydroxide complex semiconductor-like compounds which show a catalytic activity during charge. However, we found no comprehensive evaluation of the effects of cobalt on the cadmium electrode.

Another important additive to the negative electrode is polytetrafluorethylene (Teflon) (159). When added as a dispersion without sintering, it improves oxygen recombination, reducing the rate of cadmium migration and, based on information available so far, increases cell life. The faster oxygen recombination apparently results from improved three-phase interface reaction zones (188). The reasons for the longer cell life and reduced cadmium migration are not precisely known, although contributors may be the increased amount of electrolyte that becomes permissible, better distribution of electrolyte, and finer crystal structure.



## Carbonate

Carbonate ions, which are harmful contaminants, are found in concentrations ranging from one percent to over fifty percent by weight of potassium carbonate in the electrolyte. Effects of carbonates on electrochemical potential are discussed in the section on electrochemical reactions. Carbonates are introduced into the cell during manufacturing and also created as an end product of nylon-separator decomposition, consuming hydroxide ions during the process. In 18 Ah INTELSAT cells, for example, new cells had 6.0 grams of potassium carbonate per cell, and the amount increased by 0.82 grams per year (172, 61).

Small amounts of the carbonate ions will increase cadmium solubility significantly, reducing negative plate efficiency. Cadmium dissolves in carbonate solutions about eight times as much as it dissolves in KOH solutions (456), increasing the rate of cadmium migration and recrystallization, and making the crystals bigger. With high levels of contamination, carbonate choke will result. Casey describes the variation of electrochemical capacity as a function of carbonate contamination of the electrolyte, temperature, and current density (189). Cadmium electrodes of cadmium-air cells are also adversely affected by carbonate ions (187, 190, 115).

Carbonate reduces oxygen recombination, as discussed in Section 6.0. Carbonate ions will also accelerate corrosion of the nickel positive electrode (191), affecting the negative electrode in two ways: (1) An increase in positive capacity will reduce the negative-positive ratio; and (2) oxygen for the corrosion comes from the negative electrode, reducing its capacity and lowering still further the negative-positive ratio. Experts are not in agreement as to which electrode of a nickel cadmium cell is most affected by carbonate. Casey claimed that the cadmium electrode was affected most, producing a capacity loss, especially at low temperature (189). By contrast, Barney et. al. found that the positive electrode was affected the most (59), the effect on the negative electrode being voltage reduction during discharge (Fig. 9-2). One possible explanation for the discrepancy is that a very high discharge rate was used in the reference 59 study, this cell being fully discharged within five minutes. This high rate probably emphasized the effects of carbonate. Since the tested cells used were positive limited, the effect of carbonate on cadmium electrode capacity did not show up.

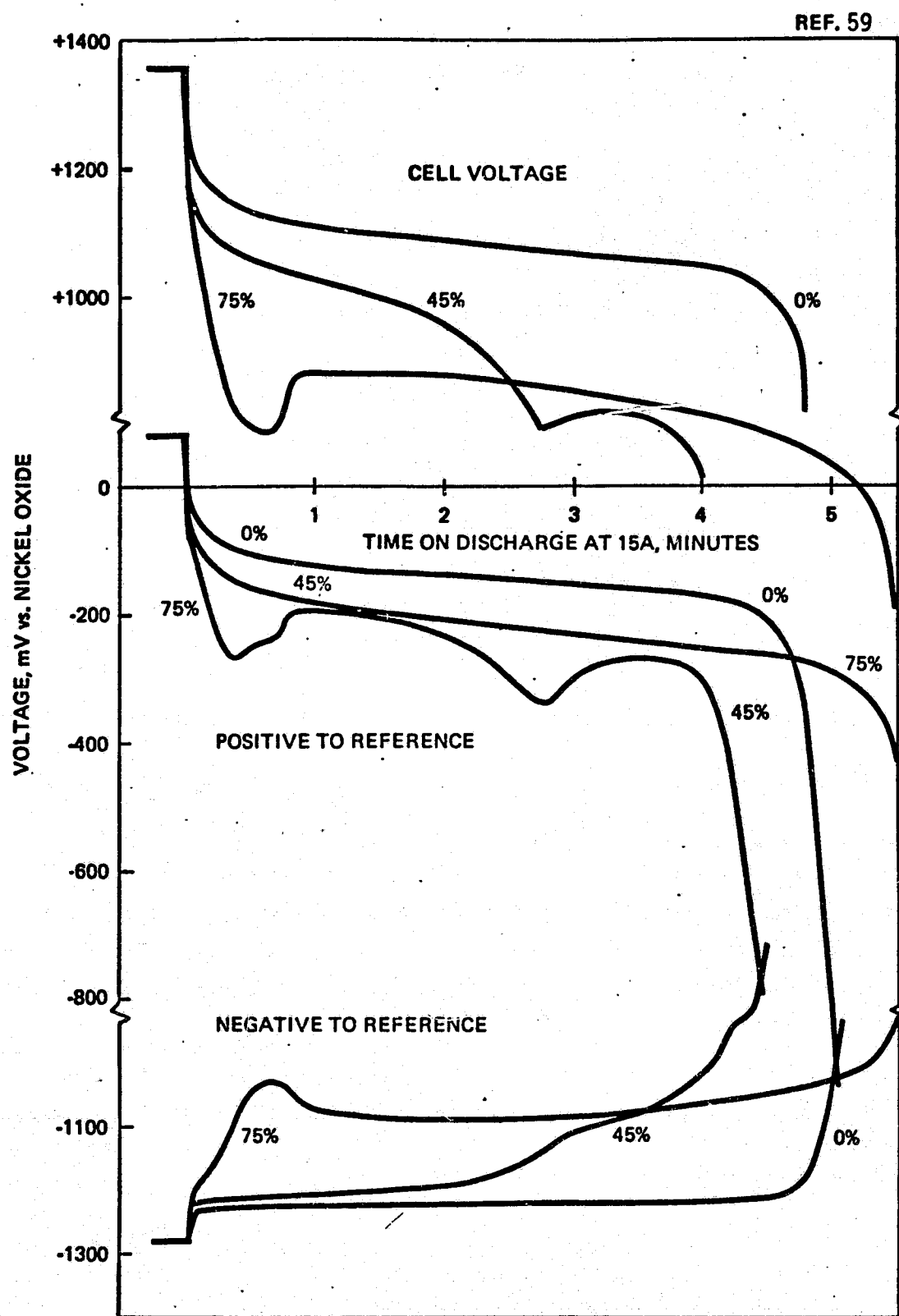


Figure 9-2. Effects of Carbonate on High Rate Discharge Voltage of Cadmium Electrode

Another effect of carbonate is increased electrophoretic mobility of  $\text{Cd}(\text{OH})_2$  (166). This can speed migration of cadmium into the separator and the positive electrode. Data and discussion on this phenomenon are provided in the section 7.0 on operation and cycling effects.

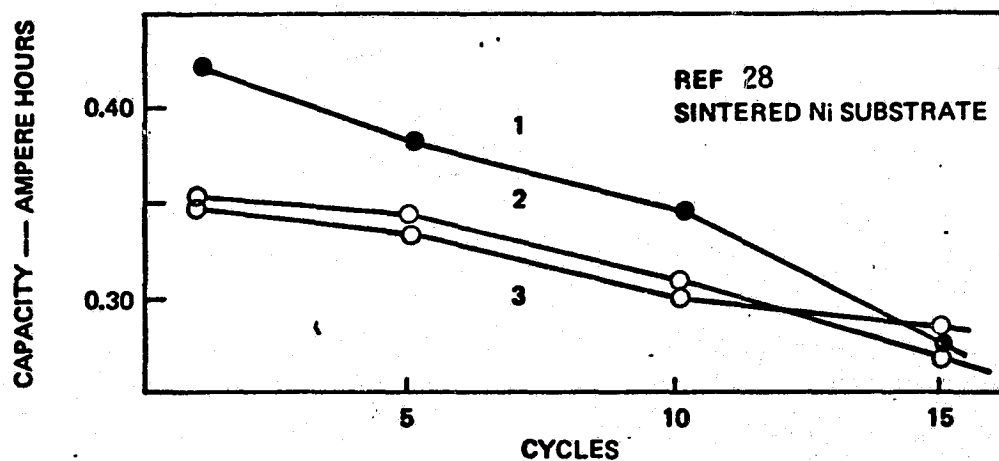
Carbonation of the cadmium electrode cannot be flushed out by cycling in KOH (189). The carbonate can be removed during manufacture by thermal decomposition at  $350^\circ\text{C}$  (100).

### Effects of Nickel Additions

After extended operation, nickel cadmium cells often begin to show a second voltage plateau on discharge, with cell voltage stepping down from 1.2 volts to about 1.05 volts, the amount of reduction depending on the discharge current. This effect is loosely called memory effect, even when it is non-reversible.

A nickel cadmium cell can lose voltage because of reversible or irreversible phenomena occurring at either the nickel positive electrode or the cadmium negative electrode. The reversible phenomena at the cadmium electrode are a recrystallization process and possibly the little-understood conversion of inactive material to active material. The irreversible voltage reduction at the cadmium electrode has been ascribed to addition of nickel into the electrode although a thorough explanation of the effects of nickel is not available. Under some conditions nickel addition appears to increase the cycle life of the cadmium electrode.

In one experiment cadmium electrodes were impregnated by thermal decomposition of cadmium acetate, and compared with similar electrodes to which 5% nickel had been added. In some of the electrodes a thermally unstable nickel salt had been mixed with cadmium acetate producing nickelic oxide and in the rest of the cadmium electrodes had been boiled in nickel chloride solution, producing nickelous hydroxide. The capacity of these electrodes during cycling is shown in Fig. 9-3. The cells were charged at  $2 \text{ mA/cm}^2$  for 17 hours and then discharged at  $4 \text{ mA/cm}^2$  to 0.8 V against a zinc electrode. Since the nickel content of the industrial cadmium electrodes used for controls is unknown, the only valid comparison that can be made is the performance of the two types of nickel additions. This comparison shows that the electrodes with nickelic oxide initially had greater capacity than electrodes with nickelous hydroxide additions, but the electrodes with nickelic oxide degraded rapidly during cycling.



ADDITIVE INTRODUCED: 1) INTO IMPREGNATING SOLUTION;  
2) DIRECTLY INTO FINISHED ELECTRODE;  
3) CONTROL (INDUSTRIAL) ELECTRODE

*Figure 9-3. Effect of Nickel Additions on Early Cycling Performance of Cadmium Electrodes*

Pozin (23) claims that irreversible voltage degradation is caused by an intermetallic nickel-cadmium compound  $\text{Ni}_5\text{Cd}_{21}$  (23). The nickel can come from corrosion of the nickel plaque during impregnation, or from small amounts of nickel impurities in solution which can co-precipitate during impregnation of the negative plates. To determine the effects of nickel, cadmium electrodes were impregnated with a nickel  $\text{Ni}^{++}$  content ranging from 0 zero percent to 27 percent, assembled into cells and tested. These cells were cycled at a discharge current of  $0.5 \text{ A/dm}^2$  to 20-30 percent of the total capacity, and then charged at 150 to 200% of the discharge capacity (23). After the 60th cycle the cells were completely discharged at  $0.25 \text{ A/dm}^2$ . Figure 9-4 shows the negative electrode potential versus  $\text{Hg/HgO}$  of plates with differing amounts of  $\text{Ni}^{+2}$  during a  $0.5 \text{ A/dm}^2$  charge in 7 N KOH containing 10 g LiOH per liter. At about 0.25 volts the +3 and +4 valence nickel oxides formed during the preceding anodic discharge are converted to bivalent nickel. The second step, at about -0.35 V, is attributed to reduction of higher nickel oxides by hydrogen peroxide, formed by reduction of oxygen dissolved in the electrolyte. At potentials of -0.9 to -1.0V the cadmium hydroxide is charged to cadmium metal. Thus, Pozin shows that the more nickel is co-precipitated with cadmium, the more noticeable is its effect on charge.

Figure 9-5 shows the negative potential during a complete discharge prior to cycling in which the plates were not only fully discharged, but were forced into oxygen evolution (23). Plates having nickel additions have a more positive voltage (giving a lower cell voltage) during the discharge, but during oxygen evolution they show a delay in reaching the oxygen potential as higher nickel oxides are formed. The negative potential during a complete discharge after cycling has the two-step behavior of plates with nickel additions (Figure 9-6). The first step corresponds to the conventional oxidation of metallic cadmium, and the second is ascribed to oxidation of cadmium alloyed with nickel. Another finding in Pozin's experiments was that there was no capacity loss in plates with nickel impurity, whereas plates that had no nickel introduced lost 20 percent of their capacity during this time.

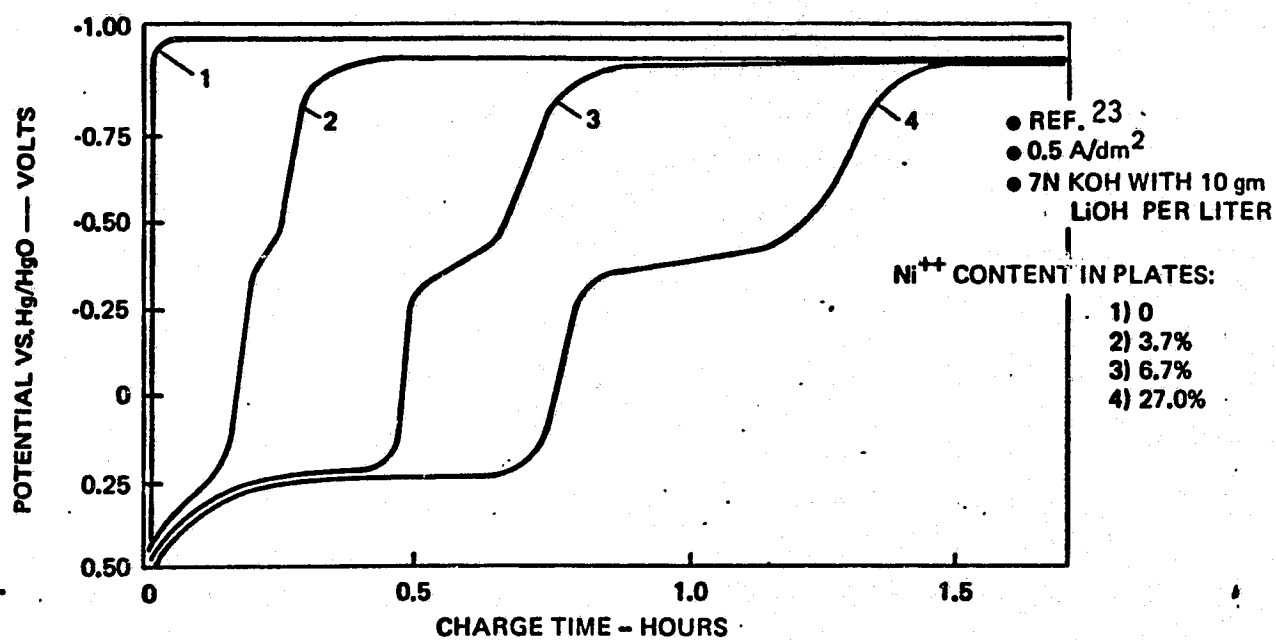
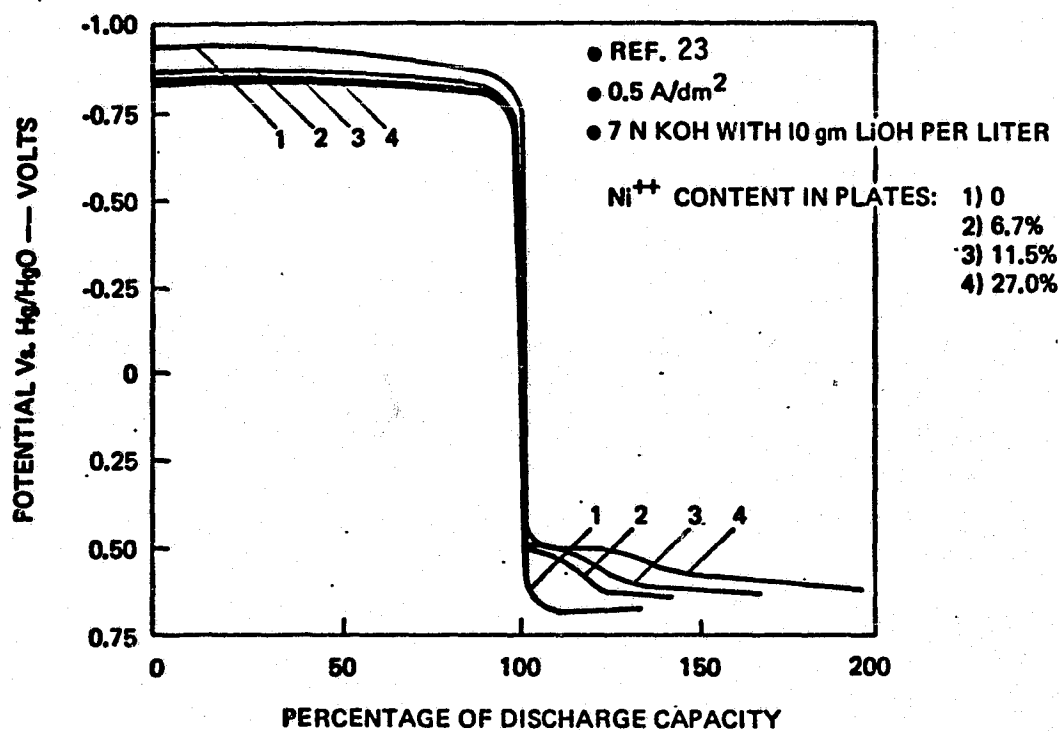
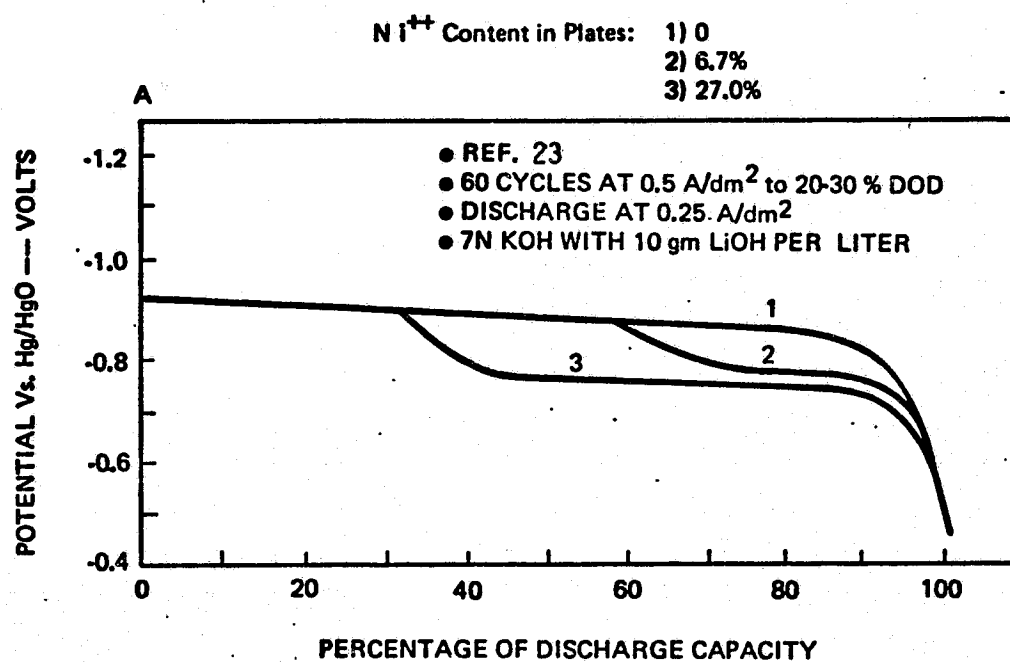


Figure 9-4. Effect of Nickel Additions on Charge of Cadmium Electrodes



*Figure 9-5. Effect of Nickel Additions on Discharge of Cadmium Electrodes Prior to Cycling*



**Figure 9-6. Effect of Nickel Additions on Discharge of Cadmium Electrodes After Prolonged Cycling**



Font confirmed Poxin's findings on the effect of nickel on the cadmium electrode (192). He used an unspecified plate loading process in which he could control the proportion of co-precipitated nickel. In one test where the plates were held at 50°C for 11 days and then discharged, he found that increased amounts of nickel not only lowered the electrode capacity but also increased the fraction of the capacity that was delivered at the lower plateau.(Fig. 9-7).

In another experiment Font impregnated one group of negative electrodes by the SAFT standard method which inherently permitted an unspecified amount of nickel to mix with the cadmium. He made the other group of cells by an unspecified process that minimized the nickel content in the cadmium plates. The negative and positive electrodes were closely matched in capacity, so that changes in the negative electrodes could be identified from the discharge performance. Font found a moderate second plateau developing after 700 cycles. After 4200 cycles, the second plateau voltage drop became severe (Fig. 9-8). The special impregnation method which left no nickel in the cadmium plates produced cells that displayed no second plateau although they lost capacity with cycling. Thus the existence of a second plateau in the discharge curve of cells having cadmium electrodes impregnated in the conventional manner can be attributed to the nickel that mixes with the cadmium.

The tests by Pozin and Font do show that nickel in the cadmium negative is harmful. However, they do not exclude the possibility that other physical or chemical effects may also help establish a second plateau.

Adding nickel hydroxide to pressed-cadmium plates used in vented cells with cellophane separators was found to reduce fading (185). This reduction, illustrated in Fig. 9-9, is just the opposite of what was experienced with nickel sintered plates. No explanation is available for this difference.

Metallic nickel powder is a common additive in pressed cadmium electrodes. It improves electrical conductivity, especially during the first formation cycle. In pocket plates, a one percent addition of nickel improved capacity by 25 percent (184).

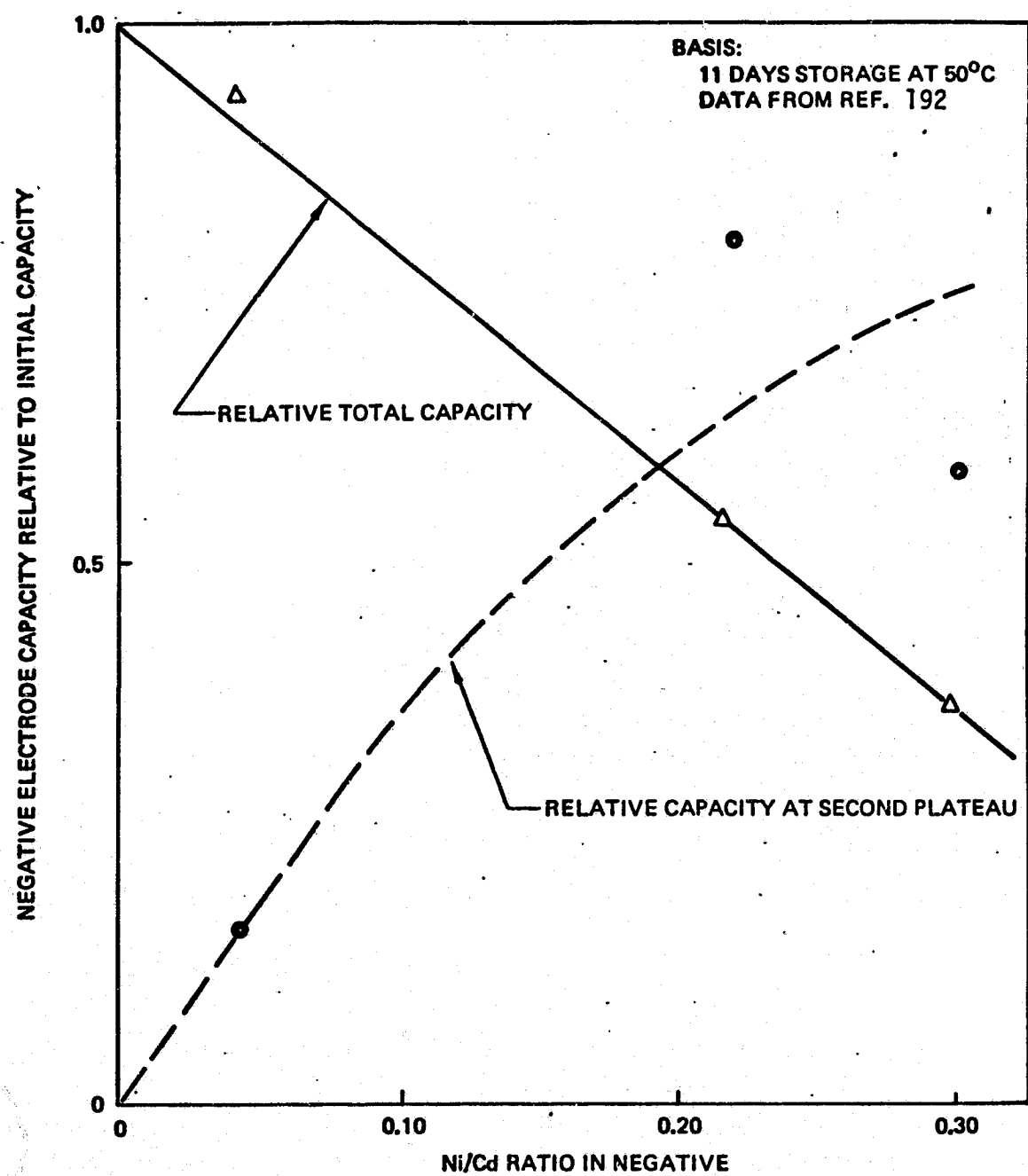


Figure 9-7. Effect of Nickel in Cadmium Electrode on Capacity Retention

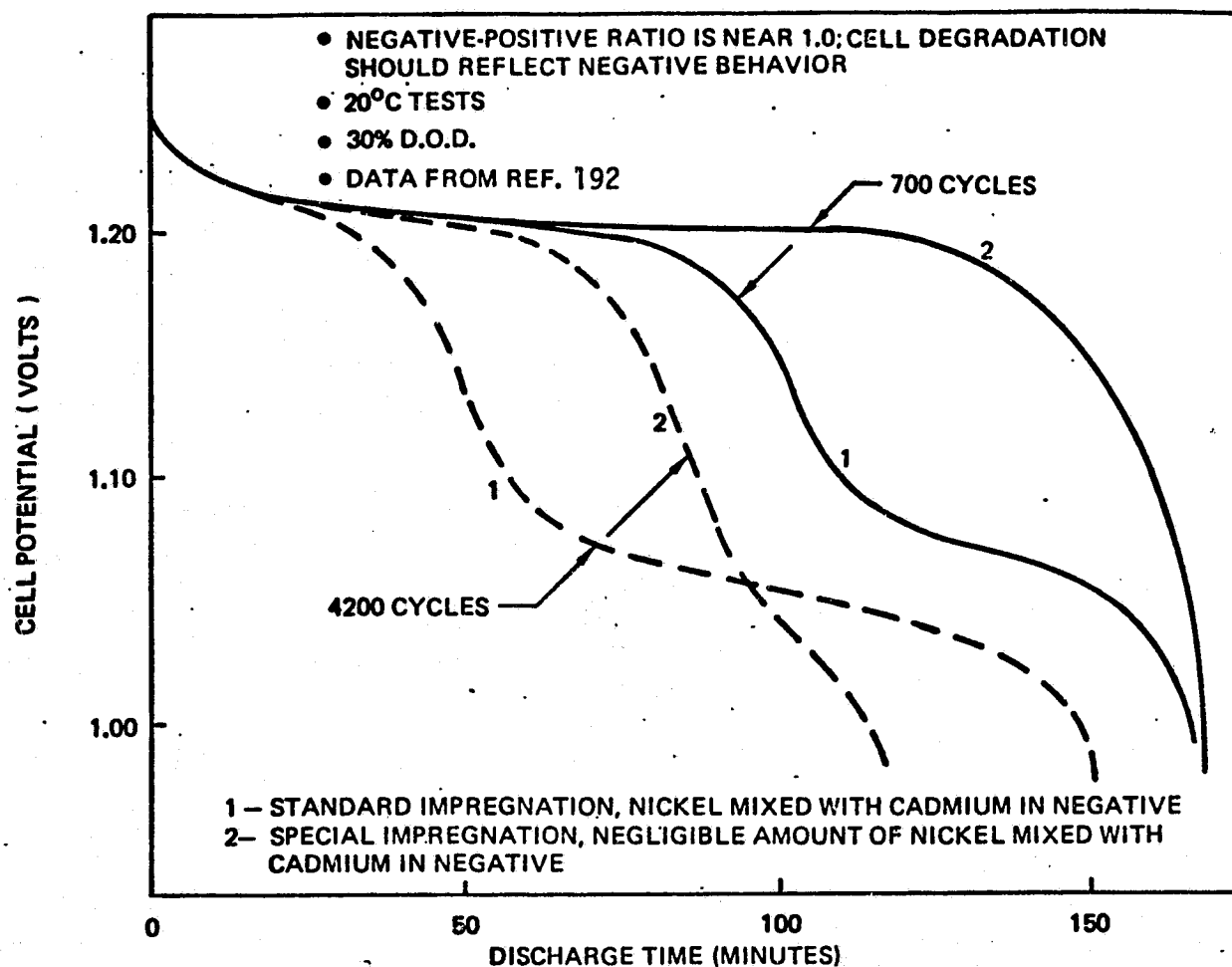


Figure 9-8. Effect of Nickel in Cadmium Negative Electrode on Voltage After Cycling

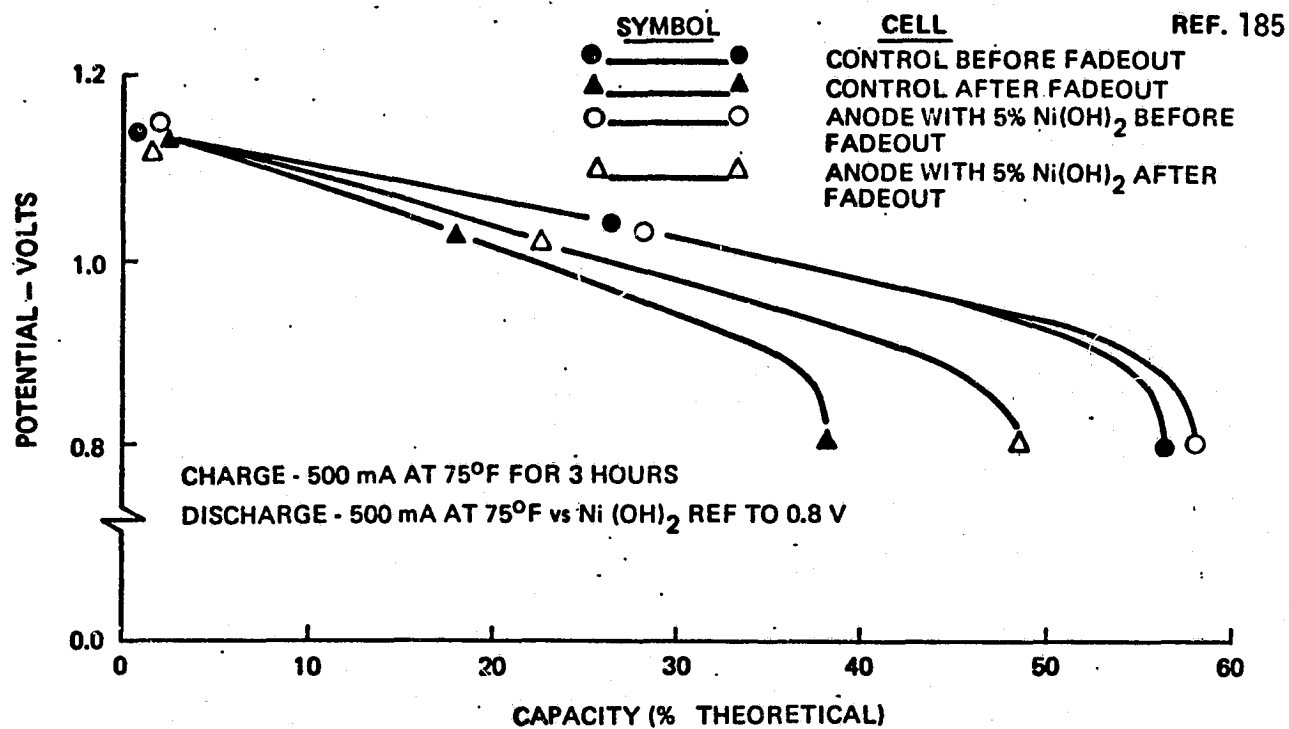


Figure 9-9. Effect of Nickel Additions on Mold-Pressed Cadmium Electrodes

Antipolar mass, when used, is generally added to the nickel positive electrode in the form of cadmium hydroxide to prevent hydrogen generation from the positive electrode during cell reversal (57). Most of the added cadmium hydroxide is converted to cadmium during reversal before oxygen evolves from the negative electrode, thus setting up an oxygen cycle during reversal. Antipolar mass in the form of nickel hydroxide can also be added to the negative plate for designs where cell could be negative limited. During reversal oxygen is evolved from the charged nickel hydroxide again setting up an oxygen cycle (193). However, this approach is little used for reversal protection, possibly because of the adverse effect that nickel additions can cause.

In summary, nickel additions produce mixed benefits. Adding nickel to cadmium electrodes of sintered construction results in cells having a step voltage drop during discharge after prolonged cycling, yet without nickel the electrode capacity falls with cycling. We need better understanding of the phenomena produced by nickel addition with the objective of finding how to avoid the voltage reduction without sacrificing capacity.

#### Other Unsatisfactory Additives and Impurities

Many other additions have been tried in attempts to improve the cadmium electrode. Solid-phase additions of oxides of silver, thallium, gallium, iron, and cobalt have been studied, but the complexities were not fully unraveled (129, 183). Oxides of nickel, iron, cobalt, and gallium were studied as liquid-phase impurities at the cadmium electrode (129, 183, 184) but no significant improvement was found.

In nickel cadmium cells with KOH electrolyte,  $\text{NO}_3$  is reduced to  $\text{NO}_2$  at the cadmium electrode with subsequent oxidation to  $\text{NO}_3$  at the nickel positive, resulting in a nitrate shuttle that causes self discharge (189). Additional investigations show that the nitrate reduction reaction is fast, whereas the nitrite oxidation reaction is slow (194). The nitrite can be further reduced by a slow reaction to ammonia which subsequently reduces to nitrogen in another slow reaction. Kinetics, rather than diffusion processes, appear to control self discharge of cells containing  $\text{NO}_3$ .

In an investigation of anodic dissolution of cadmium in aqueous solutions having neutral pH, the normal +2 valence was found to occur with  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{Ac}^-$  and  $\text{SO}_3^-$ . In solutions with  $\text{NO}_3^-$ , the apparent valence varied from 1.2 to 2.0 depending on  $\text{NO}_3^-$  concentration, current density and temperature; with  $\text{NO}_3^-$  present, local corrosion occurs, and  $\text{H}^0$  is removed from local cathodic sites on the anode surface.

Calcium and magnesium compounds are common impurities in hard water. These impurities, especially magnesium, have been found to reduce the electrochemical activity of the cadmium hydroxide, reducing discharge (130, 34). This results from an adsorption process in which the calcium or magnesium ions form saturated compounds on active centers of  $\text{Cd}(\text{OH})_2$  and thus hinder the cathodic (charge) process.

Cadmium has a high hydrogen overvoltage, which is needed to prevent hydrogen gassing. Impurities which reduce this overvoltage are therefore undesirable. Three such impurities are the calcium and magnesium found in hard water (129, 130). and silicon (129). Organic compounds, sometimes added as wetting agents to the separator, can also cause premature hydrogen gassing.

Loss of electrical capacity attributed to crystal growth and pore blockage is called fadeout. One additive that to some degree reduces fadeout of the cadmium electrode is  $\alpha\text{-Fe}_2\text{O}_3$  (187, 190, 115). A problem with this iron oxide is that it significantly reduces the capacity of the accompanying nickel positive plates because the oxygen overpotential is lowered by 50 to 80 mV (190). Titanium oxide has been tried as an extender to prevent fadeout in cadmium electrodes, but no benefit was obtained (190), although earlier reports claimed improvement (187, 115).

#### Concluding Remarks

Impurities in the negative electrode cannot be completely eliminated. Some impurities will slowly diffuse to electrode surface, and their effects may not appear until after many charge-discharge cycles. Thus, tests on the effects of impurities may not be conclusive unless they include long term cycling. Also, more appears to be known about impurities that are intentionally introduced than about impurities that come from normal manufacturing. In one experiment where impurities were carefully excluded excellent life was obtained from nickel cadmium cells (161).

## 10.0 CONCLUSIONS AND RECOMMENDATIONS

Aerospace nickel-cadmium cells can be improved by increasing their usable energy density, extending their life, and improving their operational reliability. Low cost is also desired, but cost evaluations are beyond the scope of this report. Usable energy density, life and reliability go together, for if cells can be made to degrade only slightly with use, then they can be discharged deeper.

This study has identified areas where research results are conflicting, where present knowledge is inadequate, and where additional research could be worthwhile. These areas where technology has not addressed a problem or where a mechanism cannot be agreed upon are impediments to the achievement of a reproducible, reliable, lightweight and longlife negative electrode, and are identified and discussed below.

1. Many questions about plaque structures have not been resolved. Recent studies at Bell Laboratories indicate that careful and continuous control of plaque parameters (e.g., strength, pore size) is required for long life cells. Manufacturers generally regard plaque fabrication methods and controls as proprietary, so information is lacking for aerospace cells. As a starting point, it is suggested that JPL evaluate existing test methods and then conduct comparative tests on plaques from various manufacturers. In addition to testing unimpregnated plaque, the active material can be extracted from cadmium plates to leave the plaque intact for testing.

2. Many variations in cadmium-electrode manufacturing processes have been identified, but a detailed evaluation of these methods has not been found. For example, lightweight electrodes can be made by pressing mixtures of cadmium, Teflon, nickel, and/or graphite onto suitable substrates. While a preliminary study indicates that higher energy density is obtained, a thorough evaluation in an extended cycle life test has not been found.

3. The choice of light loading or heavy loading of active material into the plaque during imgregration has not been resolved. Some reports indicate that light loading improves cycle life, but possibly at the expense of energy density. Nevertheless, if a lightly loaded cell is long lasting and can be operated at greater depth of discharge, then there is an overall improvement. The effects of loading on degradation rates of cadmium electrodes should be evaluated to provide a basis for trades between life and weight.

4. Electrode geometry seems to be a key factor that affects electrode efficiency, fading and oxygen recombination. A high void volume is especially important. However, the cadmium electrode has not been characterized by well defined tests. Such tests would permit comparison of plates of different design, plates from different lots, and plates that have been in operation for varying lengths of time. Parameters that could be worthwhile include the Thiele parameter, a choking factor based on the Bruggeman-Baron equation, Casey's choking index, and Selanger's electrode activity.

5. The role of silver in oxygen recombination is not well understood. Although silver is being used in some aerospace cells, little data could be found on performance improvement, cycling effects, effects of impurities, or on other effects silver has on the electrode. In fact, some data suggest that silver may be partly responsible for cadmium electrode degradation observed in tests.

6. The fundamental oxygen recombination processes at the cadmium electrode are not adequately known. Existing data suggest that the process is diffusion limited, more specifically diffusion of oxygen to the reaction site. The catalytic effect of silver, however, suggests that diffusion or decomposition of peroxide could be the rate-limiting process. Also, there is no explanation for the improvement in recombination during long trickle charge.



7. Cadmium electrodes made from nickel fiber plaques are substantially more prone to shorts than are electrodes made from conventional plaques. An insight into the mechanism of shorting might be obtained from learning why this is so.
8. Little data substantiates the generally believed relationship between cadmium migration and shorting. It is not known what the mechanism is for conversion of cadmium species in the separator to metallic cadmium.
9. Very little of the voluminous life data on nickel cadmium cells provides good insight into the cadmium electrode cycle-life behavior. Procedures to be used on future NASA/JPL tests should be reviewed to assure that the needed information will be obtained. COMSAT analysis procedures are suggested as an interim model.
10. No information is available on hydrogen gassing characteristics of non-nickel materials connected to the negative electrode. This includes the header, parts of the negative terminal, and in some designs the cell case interior. These materials which should have hydrogen overvoltages less than that of cadmium, may gas more readily than the negative electrode.
11. Data are not available on crystal ripening rates for the cadmium electrode. Such data would be valuable in establishing maximum durations of cell storage between reconditioning events.
12. Data are not available on the rates at which large  $\text{Cd(OH)}_2$  crystals shrink during overcharge. Such data would be valuable in establishing reconditioning procedures.
13. No data could be found on the local electrolyte concentration changes and gradients that occur at the reaction sites. This information would permit analyses and interpretation of some of the phenomena that occur at the cadmium electrode.

14. During charge-discharge cycling the active material migrates from the inside of the plaque to the outside. One might load the center of the plaque more heavily than the outer regions to anticipate this migration. No one seems to have investigated this approach for aerospace cells, although there is an indication of success with special vented cells.

15. Cadmium hydroxide produced during oxygen recombination has been claimed by some to be especially active, and by others to be especially inactive. Available data do not support either claim.

16. The hydrogen recombination capability of nickel cadmium cells is inadequately defined. Data are available from only one test, and this did not use typical cell construction. Measuring recombination rates would be worthwhile and relatively easy to do.

17. The three known allotropic forms of metallic cadmium are the alpha, beta and gamma forms. No studies on cadmium electrodes have determined which form predominates in electrodes, whether there is any difference in electrochemical activities, and which operating conditions favor the production of each allotropic form.

18. Calcium and magnesium are especially harmful to the cadmium electrode and should not be present as impurities. Impurity analyses of aerospace cells should include these two ions.

19. Indium additions have improved the energy density and efficiency of cadmium electrodes. This technology should be evaluated for improving aerospace cells.

20. Nickel additions to cadmium electrodes produce mixed benefits, preventing capacity fall-off with cycling, yet causing a voltage reduction with cycling. A better understanding of this phenomenon is needed, with the objective of finding how to avoid the voltage reduction without sacrificing capacity.

21. Pulse charging can improve the morphology of degraded cadmium electrodes. The mechanism for this is not known. Since even one pulse charging cycle makes a big improvement, there may be many ways of effectively using pulse charging for aerospace batteries, including ground conditioning, intermittent in-flight use, or continuous in-flight use. Further study of pulse charging would be worthwhile.

22. The inclusion of Teflon particles in cadmium negative plates appears to benefit plate life. Such Teflon inclusion is likely to become one of the standard features in aerospace cells. Therefore, more information is needed on the physical effects of this additive, its effect on weight, the risks and harmful effects that can occur, the manufacturing steps that are critical and must be controlled carefully, and the tests that are needed to monitor and evaluate Teflon addition processes. To some extent, the Teflon compensates for deficiencies in the electrode, and should therefore give clues to ways the plaque substrate can be improved. Also, cells with Teflonated negatives can tolerate more electrolyte, but it is not certain that cells are better off with the added electrolyte.

23. Information is not available on how often cells on test are negative limited, for there is no simple negative-limit test. Use of cell voltage-current characteristics as the voltage passes through zero is suggested as an approach for determining the negative-limit condition.

24. This study has shown that substantial research has been devoted to understanding the cadmium electrode. A similar study directed to the positive electrode and total nickel-cadmium cell would help establish the status of research in aerospace battery technology.

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#### NEW TECHNOLOGY

This report contains a review of the status of research regarding the cadmium electrode. No reportable items of new technology have been identified pursuant to the new technology provisions of the contract.